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ANNUAL REPORTS

ON THE

PROGRESS OF CHEMISTRY.

ANNUAL REPORTS
ON THE
PROGRESS OF CHEMISTRY
FOR 1930.

ISSUED BY THE CHEMICAL SOCIETY.

16859

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Vol. XXVII.

LONDON:
THE CHEMICAL SOCIETY
1931.

PRINTED IN GREAT BRITAIN BY
RICHARD CLAY & SONS, LIMITED,
BUNGAY, SUFFOLK.

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TABLE OF ABBREVIATIONS EMPLOYED IN THE REFERENCES.

Abbreviated Title.	FULL TITLE.
A.	Abstracts in Journal of the Chemical Society (until 1925) or in British Chemical Abstracts,* Section A.
Abs. Theses Univ. Chicago (Sci. Ser.)	Abstracts of Theses, University of Chicago (Science Series).
Amer. Inst. Met. Eng. Tech. Pub.	American Institute of Mining and Metallurgical Engineers Technical Publications.
Amer. J. Bot.	American Journal of Botany.
Amer. J. Pharm.	American Journal of Pharmacy.
Amer. J. Physiol.	American Journal of Physiology.
Amer. J. Sci.	American Journal of Science.
Amer. Min.	American Mineralogist.
Amer. Rev. Tuberculosis	American Review of Tuberculosis.
Anal. Asoc. Quím. Argentina	Anales de la Asociacíon Química Argentina.
Anal. Fis. Quím.	Anales de la Sociedad Espanõla Física y Química.
Analyst	The Analyst.
Annalen	Justus Liebig's Annalen der Chemie.
Ann. Acad. Brasil. Sci.	Annals da Academia Brasileira de Sciencias.
Ann. Appl. Bot.	Annals of Applied Botany.
Ann. Bot.	Annals of Botany.
Ann. Chim.	Annales de Chimie.
Ann. Chim. Appl.	Annali di Chimica Applicata.
Ann. Inst. Anal. Phys. Chem.	Annales de l'Institute d'Analyse physico-chimique, Leningrad.
Ann. Inst. Platine	Annales de l'Institut de Platine et des autres Métaux précieux.
Ann. Physik	Annalen der Physik.
Ann. Reports	Annual Reports of the Chemical Society.
Apoth.-Ztg.	Apotheker-Zeitung.
Arch. Eisenhüttenw.	Archiv für das Eisenhüttenwesen.
Arch. ges. Physiol.	Archiv für die gesamte Physiologie des Menschen und der Tiere (Pflügers Archives).
Arch. Pharm.	Archiv der Pharmazie.
Arch. Physique biol.	Archives de Physique biologique.
Arch. Sci. Biol. St. Petersburg	Archives des Sciences biologiques, St. Petersburg.
Arch. Sci. phys. nat.	Archives des Sciences physiques et naturelles.
Arhiv Hemiju	Arhiv za Hemiju i Farmaciju.
Arkiv Kemi, Min., Geol.	Arkiv för Kemi, Mineralogi och Geologi.
Arq. Seminario Est. Galegos	Arquivos do Seminario d'Estudos Galegos.
Astrophys. J.	Astrophysical Journal.
Atti R. Accad. Lincei	Atti (Rendiconti, Memorie) della Reale Accademia Nazionale dei Lincei, classe di scienze fisiche, matematiche e naturali, Roma.
B.	British Chemical Abstracts,* Section B.
Bán. Koh. Lapok	Bányászati és Kohászati Lapok.
Ber.	Berichte der deutschen Chemischen Gesellschaft.
Biochem. J.	The Biochemical Journal.
Biochem. Z.	Biochemische Zeitschrift.
Biol. Reviews	Biological Reviews.
Brennstoff.-Chem.	Brennstoff-Chemie.
Bul. Soc. Chim. România	Buletinul Societãtei de Chimie din România.
Bull. Acad. Polonaise	Bulletin Internationale de l' Académie Polonaise des Sciences et des Lettres.
Bull. Acad. roy. Belg.	Académie royale de Belgique.—Bulletin de la Classe des Sciences.
Bull. Acad. Sci. Roumaine	Bulletin de la Section Scientifique de l'Académie Roumaine.
Bull. Acad. Sci. Leningrad.	Bulletin de l'Académie des Sciences, Leningrad.
Bull. Acad. Sci. U.S.S.R.	Bulletin de l'Académie des Sciences de l'Union des Républiques Soviétiques Socialistes.
Bull. Chem. Soc. Japan	Bulletin of the Chemical Society of Japan.

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* The year is not inserted in references to 1930.

Abbreviated Title.	FULL TITLE.
Bull. Inst. Phys. Chem. Res. Tokyo	Bulletin of the Institute of Physical and Chemical Research, Tokyo.
Bull. Soc. chim.	Bulletin de la Société chimique de France.
Bull. Soc. chim. Belg.	Bulletin de la Société chimique de Belgique.
Bull. Soc. Chim. biol.	Bulletin de la Société de Chimie biologique.
Bull. Soc. franç. Min.	Bulletin de la Société française de Minéralogie.
Bull. Soc. Pharm. Bordeaux	Bulletin des Travaux de la Société de Pharmacie de Bordeaux.
Bull. U.S. Geol. Survey	Bulletin of the United States Geological Survey.
Bull. U.S. Nat. Museum	Bulletin of the United States National Museum.
Bull. Wagner Inst. Sci.	Bulletin of the Wagner Free Institute of Science of Philadelphia.
Bur. Stand. J. Res.	Bureau of Standards Journal of Research.
Canadian J. Res.	Canadian Journal of Research.
Centr. Min.	Centralblatt für Mineralogie, Geologie, und Paläontologie.
Chem. and Ind.	Chemistry and Industry.
Chem. Erde	Chemie der Erde.
Chem. Listy	Chemické Listy pro Vědu a Průmysl. Organ de la "Ceská chemická Společnost pro Vědu a Průmysl."
Chem. News	Chemical News.
Chem. Reviews	Chemical Reviews.
Chem. Weekblad	Chemisch Weekblad.
Chem. Zentr.	Chemisches Zentralblatt.
Chem.-Ztg.	Chemiker-Zeitung.
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
Compt. rend. Soc. Biol.	Comptes rendus hebdomadaires de Séances de la Société de Biology.
Econ. Geol.	Economic Geology.
Gazzetta	Gazzetta chimica italiana.
Giorn. Chim. Ind. Appl.	Giornale di Chimica Industriale ed Applicata.
Helv. Chim. Acta	Helvetica Chimica Acta.
Helv. Phys. Acta	Helvetica Physica Acta.
Ind. Eng. Chem.	Industrial and Engineering Chemistry.
Ind. Eng. Chem. (Anal.)	Industrial and Engineering Chemistry: Analytical Edition.
J.	Journal of the Chemical Society.
J. Agric. Res.	Journal of Agricultural Research.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Amer. Med. Assoc.	Journal of the American Medical Association.
J. Amer. Pharm. Assoc.	Journal of the American Pharmaceutical Association.
J. Appl. Chem. Russia	Zhurnal prikladnoi Chimii.
J. Assoc. Off. Agric. Chem.	Journal of the Association of Official Agricultural Chemists.
J. Bact.	Journal of Bacteriology, Baltimore.
J. Biol. Chem.	Journal of Biological Chemistry.
J. Chem. Ind. Russia	Journal of Chemical Industry of Russia.
J. Chim. physique	Journal de Chimie physique.
J. Czech. Chem. Comm.	Journal of Czechoslovak Chemical Communications.
J. Dept. Agric. Kyushu	Journal of the Department of Agriculture, Kyushu Imperial University.
J. Elisha Mitchell Sci. Soc.	Journal of the Elisha Mitchell Scientific Society.
J. Franklin Inst.	Journal of the Franklin Institute.
J. Gen. Physiol.	Journal of General Physiology.
J. Geol.	Journal of Geology.
J. Indian Chem. Soc.	Quarterly Journal of the Indian Chemical Society.
J. Indian Inst. Sci.	Journal of the Indian Institute of Science.
J. Inst. Metals	Journal of the Institute of Metals.
J. Marine Biol. Assoc.	Journal of the Marine Biological Association of the United Kingdom.

Abbreviated Title.	FULL TITLE.
J. Pharm. Chim.	Journal de Pharmacie et de Chimie.
J. Pharm. Soc. Japan.	Journal of the Pharmaceutical Society of Japan, (Yakugakuzasshi).
J. Phys. Radium	Journal de Physique et le Radium.
J. Physical Chem.	Journal of Physical Chemistry.
J. pr. Chem.	Journal für praktische Chemie.
J. Roy. Tech. Coll. Glasgow	Journal of the Royal Technical College (Glasgow).
J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia.
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
J. Soc. Chem. Ind. Japan	Journal of the Society of Chemical Industry, Japan. (Kōgyō Kwagaku Zasshi.)
J. Soc. Glass Tech.	Journal of the Society of Glass Technology.
J. Washington Acad. Sci.	Journal of the Washington Academy of Sciences.
Jahrb. Min., Beil.-Bd.	Neues Jahrbuch für Mineralogie, Geologie und Paläontologie, Beilage-Band.
K. Svenska Vetenskapsakad. Handl.	Kongliga Svenska Vetenskaps Akademiens Handlingar.
Kgl. Danske Videnskabs. Selsk. Math.-phys. Med.	Kongelige Danske Videnskabernes Selskab, Mathematisk-fysiske Meddelelser.
Kolloidchem. Beih.	Kolloidchemische Beihefte.
Kolloid-Z.	Kolloid-Zeitschrift.
Mem. Coll. Sci. Kyoto.	Memoirs of the College of Science, Kyoto Imperial University.
Mikrochem.	Mikrochemie.
Min. Mag.	Mineralogical Magazine and Journal of the Mineralogical Society.
Mitt. Lebensm. Hyg.	Mitteilungen aus dem Gebiete der Lebensmitteluntersuchung und Hygiene.
Monatsh.	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
N.J. Agric. Exp. Sta. Bull.	New Jersey Agricultural Experimental Stations Bulletin.
Nach. Ges. Wiss. Göttingen.	Nachrichten von der Gesellschaft der Wissenschaften zu Göttingen.
Naturwiss.	Die Naturwissenschaften.
Natuurwetensch. Tijds.	Natuurwetenschappelijk Tijdschrift.
New Phyt.	New Phytologist.
Nuovo Cim.	Il Nuovo Cimento.
Oesterr. Chem.-Ztg.	Oesterreichische Chemiker-Zeitung.
Pflügers Arch.	Archiv für die gesamte Physiologie des Menschen und der Tiere.
Pharm. Weekblad	Pharmaceutisch Weekblad.
Pharm. Zentr.	Pharmazeutische Zentralhalle.
Pharm.-Ztg.	Pharmazeutische Zeitung.
Phil. Mag.	Philosophical Magazine (The London, Edinburgh and Dublin).
Phil. Trans.	Philosophical Transactions of the Royal Society of London.
Philippine J. Sci.	Philippine Journal of Science.
Physical Rev.	Physical Review.
Physikal. Z.	Physikalische Zeitschrift.
Plant Physiol.	Plant Physiology.
Planta	Zeitschrift für wissenschaftliche Biologie. Abteilung E. Planta. Archiv für wissenschaftliche Botanik.
Proc. Acad. Sci. Amsterdam	Proceedings of the Royal Academy of Sciences of Amsterdam (English Version).
Proc. Biochem. Soc.	Chemistry and Industry (Proceedings of Biochemical Society).
Proc. Camb. Phil. Soc.	Proceedings of the Cambridge Philosophical Society.
Proc. Imp. Acad. Tokyo	Proceedings of the Imperial Academy of Japan.
Proc. K. Akad. Wetensch. Amsterdam	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings (English version).

Abbreviated Title.	FULL TITLE.
Proc. Leeds Phil. Soc.	Proceedings of the Leeds Philosophical and Literary Society (Scientific Section).
Proc. Nat. Acad. Sci.	Proceedings of the National Academy of Sciences.
Proc. Nova Scotia Inst. Sci.	Proceedings of the Nova Scotia Institute of Science.
Proc. Physical Soc.	Proceedings of the Physical Society of London.
Proc. Roy. Soc.	Proceedings of the Royal Society.
Proc. U.S. Nat. Museum	Proceedings of the United States National Museum.
Proc. Univ. Durham Phil. Soc.	Proceedings of the University of Durham Philosophical Society.
Przemysł Chem.	Przemysł Chemiczny.
Quart. J. Geol. Soc.	Quarterly Journal of the Geological Society.
Quim. e Ind.	Quimica e Industria.
Rec. trav. chim.	Recueil des travaux chimiques des Pays-Bas et de la Belgique.
Rev. gén. Colloïd.	Revue génerale des Colloïdes.
Rev. Sci. Instr.	Review of Scientific Instruments.
Rocz. Chem.	Roczniki Chemji organ Polskiego Towarzystwa Chemicznego.
Sci. Papers Inst. Phys. Chem. Res. Tokyo	Scientific Papers of the Institute of Physical and Chemical Research, Tokyo.
Sci. Rep. Tôhoku Imp. Univ.	Science Reports, Tôhoku Imperial University.
Semana méd.	La Semana médica (Buenos Aires).
Sitzungsber. Akad. Wiss. Wien.	Sitzungsberichte der Akademie der Wissenschaften, Wien.
Sitzungsber. Preuss. Akad. Wiss. Berlin	Sitzungsberichte der Preussischen Akademie der Wissenschaften zu Berlin.
Suomen Kem.	Suomen Kemistilehti Acta Chemica Fennica.
Svensk Farm. Tidskr.	Svensk Farmaceutisk Tidskrift.
Svensk Kem. Tidskr.	Svensk Kemisk Tidskrift.
Tidsskr. Kjemi Berg.	Tidsskrift for Kemi og Bergvaesen.
Trans. Amer. Electrochem. Soc.	Transactions of the American Electrochemical Society.
Trans. Canad. Inst. Min. Met.	Transactions of the Canadian Institute of Mining and Metallurgy and of the Mining Society of Nova Scotia.
Trans. Ceramic Soc.	Transactions of the Ceramic Society.
Trans. Faraday Soc.	Transactions of the Faraday Society.
Trans. Roy. Soc. Canada	Transactions of the Royal Society of Canada.
Tsch. Min. Petr. Mitt.	Tschermaks mineralogische und petrographische Mitteilungen.
Ukraine Chem. J.	Ukraine Chemical Journal.
U.S. Bur. Stand. Res. Paper	Research Papers of the U.S. Bureau of Standards.
Verh. Geol. Bundesanst. Wien	Verhandlungen der Geologischen Bundesanstalt, Wien.
Vers. K. Akad. Amsterdam	Verslag Koninklijke Akademie Wetenschappen te Amsterdam.
Wiss. Veröff. Siemens-Konz.	Wissenschaftliche Veröffentlichungen aus dem Siemens-Konzern.
Z. anal. Chem.	Zeitschrift für analytische Chemie.
Z. angew. Chem.	Zeitschrift für angewandte Chemie.
Z. anorg. Chem.	Zeitschrift für anorganische und allgemeine Chemie.
Z. Elektrochem.	Zeitschrift für Elektrochemie.
Z. Geophys.	Zeitschrift für Geophysik.
Z. Krist.	Zeitschrift für Kristallographie.
Z. Metallk.	Zeitschrift für Metallkunde.
Z. Pflanz. Düng.	Zeitschrift für Pflanzenernährung und Düngung.
Z. Physik	Zeitschrift für Physik.
Z. physikal. Chem.	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
Z. physiol. Chem.	Hoppe-Seyler's Zeitschrift für physiologische Chemie.
Z. tech. Physik.	Zeitschrift für technische Physik.
Z. Ver. deut. Zucker-Ind.	Zeitschrift des Vereins der deutschen Zucker-Industrie.

ANNUAL REPORTS

ON THE

PROGRESS OF CHEMISTRY.

GENERAL AND PHYSICAL CHEMISTRY.

By necessity, and by the sanction of custom, this Report is confined to the discussion of a few matters, and can only hope to reflect some of the dominant motives. One of these has been the interpretation of old-established chemical ideas in terms of the physics of the quantum theory. Although some of the physical theories have their limitations, and could perhaps never have been constructed unless the chemical facts had already been well understood, their introduction has been not only fruitful but illuminating. No excuse, therefore, is made for the space devoted to them in the Report: but an attempt has been made to show where they are purely formal or even arbitrary, and where they contribute qualitatively new ideas. The chances of success of such an attempt are not great, but it is one which ought to be made. Another matter to which intensive study has recently been devoted is the elucidation of so-called elementary processes, by which is meant the atomic and molecular mechanisms of chemical changes: this aspect has been rather fully represented in the following pages.

Regret must be expressed at the unavoidable omission of reference to systematic thermodynamics, to the analysis of inorganic crystal structures, to new methods of measurement, to the chemistry of the photographic process—on all of which matters valuable papers have been published—and, especially, to many examples illustrating themes which have been discussed too recently in these Reports to be profitably re-opened at the present moment.

The Quantum Mechanical Treatment of Chemical Forces.

During the last few years the wave mechanical and quantum mechanical theories of the electron, the atom, and the interaction between atoms have caused a profound change in physical ideas. It is not an inappropriate moment to consider what corresponding modifications in our views about fundamental problems of chemistry have resulted from or accompanied these new physical conceptions.

In the first place, it must be said that the electron and the atom do not at all cease to play their traditional chemical rôles as definite and essentially discrete entities. It is true that a beam of electrons can be diffracted in a manner analogous to a train of waves of wave-length h/mv, mv being the momentum of one of the electrons. Several further convincing demonstrations of this have been forthcoming since the last Report : indeed A. Dauvillier [1] describes a method by which the diffraction of an electron beam by a film of microcrystalline zinc oxide can be rendered visible, and the de Broglie wave-length relation demonstrated by changing the speed of the electrons. Not only electrons, but protons and atoms appear to be capable of diffraction. I. Estermann and O. Stern,[2] following up work by F. Knauer and Stern,[3] have shown that, when a ray of helium atoms or hydrogen molecules is incident on a cleavage face of lithium fluoride, the intensity of the rays scattered in different directions corresponds exactly to the diffraction of waves by a grating. If the distance apart of two like ions in the crystal is taken as the grating constant, the wave-length can be calculated. It is found to vary with the speed and mass of the particles in accordance with the de Broglie equation $\lambda = h/mv$. Investigations on the reflexion of hydrogen atoms from crystals have been made by A. J. Dempster [4] and T. H. Johnson.[5] A summary of all diffraction experiments is given by S. Kikuchi.[6]

But the most satisfactory interpretation of these phenomena seems to be a statistical one, the relative amplitude of a wave function at any point expressing the relative numbers of scattered electrons or atoms which occur in a small volume element in the neighbourhood of that point.* The fact that the probability of scattering in a given direction varies in a wave-like manner is, of course, a new truth of fundamental importance, but from the chemical point of view it is better to regard the wave-like character of electrons and protons as something determining where they will go rather than as describing what they are.

Applied to systems more complex than a single electron or proton, wave mechanics (and equally Heisenberg's quantum mechanics) is in the first instance a formal calculus for expressing the older quantum laws in a more convenient, more correct, and much completer way than was possible before. The older laws restricted the possible values for the energy of a system by the arbitrary introduction of whole-number relationships: the new method derives the whole numbers in another way. It asserts that the possible states of a system are determined by a function, usually denoted by ψ, which does not represent anything directly perceptible or measurable, but which satisfies an equation for the propagation of waves. Certain of the mathematical prescriptions involved in the calculations, *e.g.*, the method of " normalisation " (or the commutation rule in Heisenberg's mechanics), are not rules which suggest themselves naturally to physical intuition, but are directly designed to retain the Bohr and Planck relations ($\Delta E = h\nu$). Moreover, the fact that in complex systems the " waves " are propagated in as many dimensions as there are co-ordinates, shows that we are dealing with something without so-called physical reality: thus it is necessary to be clear about the fact that the waves do not substitute a new physical picture for the older pictures used in chemistry. But the important fact is this: the *behaviour* of systems is determined or described by a *function* which has the character of a wave function, and, in particular, which vibrates with a frequency equal to E/h, where E is the energy of the system in the state considered.

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[1] *Nature*, 1930, **125**, 50; *A.*, 129.

[2] *Z. Physik*, 1930, **61**, 95; *A.*, 515.

[3] *Ibid.*, 1929, **53**, 779; *A.*, 1929, 490.

[4] *Nature*, 1930, **125**, 51, 741; *A.*, 129, 835.

[5] *Physical Rev.*, 1928, [ii], **31**, 1122; *A.*, 1929, 1358; *J. Franklin Inst.*, 1929, **207**, 629, 639; *A.*, 1930, 514.

[6] *Physikal. Z.*, 1930, **31**, 777.

* The analogous synthesis of the undulatory and quantum characters of light is also becoming a commonplace of physics.

Schrödinger's wave equation [7] is

$$\Sigma\left\{\frac{1}{m}\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}\right)\right\}+\frac{8\pi^2}{h^2}(E-U)\psi=0;$$

E is the total energy, and U is the potential energy.

The point of the new mathematical formulation lies in the fact that the wave equation has solutions only for certain definite values of the energy (proper values or characteristic values) which represent the energy levels of the quantum theory.

Now, although primarily a device for specifying possible energy states, and the conditions of transition from one to another, rather than a new physical theory, Schrödinger's function, vibrating with frequency E/h, confers certain qualitative characters upon molecular systems which were not accounted for by older theories.* The most important of these is the possibility of what is known as quantum mechanical resonance, which has led to an interpretation of the forces involved in chemical combination.[8]

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[7] Compare, *e.g.*, Bloch, " L'Ancienne et la Nouvelle Théorie des Quanta," Paris, 1930.

* Heisenberg's mechanics, although formally different in its postulates, is equivalent to Schrödinger's, and operates with vibrating quantities as its fundamental magnitudes.

Consider two hydrogen atoms. The possible energy states of the two isolated atoms are naturally identical, and are determined by the solution of a ψ-equation containing the potential energy of one atom; ψ vibrates with frequency $\nu = E/h$. Now if the two hydrogen atoms are interacting with one another they must be treated as one system, the total potential energy which is inserted in the equation being modified by the electrostatic forces. Since the frequencies associated with the two separate atoms are identical, a phenomenon exactly analogous to resonance occurs, and instead of the joint system being associated with the same frequency as the two isolated atoms, ν assumes two values $\nu \pm \nu'$, a well-known effect of resonance.* Since $E = h\nu$, there are two solutions to the wave equation expressing the possible states of a pair of hydrogen atoms, the corresponding energies being $E_0 + e$ and $E_0 - e$, where E_0 is the value for two atoms, not exerting any action on each other. If, for some assigned distance apart of the two atoms, the joint system has a smaller energy than the separate atoms, union to a molecule takes place. However, the quantum theory by itself gives no reason to prefer the solution with smaller energy to that with larger energy corresponding to a repulsion between the atoms. Further progress depends upon the application of the Pauli principle. This principle in its earlier form stated that no two electrons in a molecule can have all four quantum numbers the same, and it has a strong empirical foundation in the facts of spectroscopy. In terms of wave mechanics it asserts that all states of a molecule are excluded of which the Schrödinger functions depend upon several electrons (or protons) in the same way. For example, in the present problem the two solutions correspond, roughly speaking, to vibrations in the same phase (symmetrical) and in phases differing by π (antisymmetrical). The symmetrical solution is the one which can give combination; but it would be forbidden by the Pauli principle unless the two electrons concerned could differ in some other respect from one another. They can, however, have opposite spins. Two hydrogen atoms with oppositely spinning electrons can unite to a molecule : two with parallel spins repel each other. Thus the chemical bond appears as a pair of electrons with opposite spins. Since only two directions of spin are possible, the saturation of chemical valencies receives an interpretation.

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[8] W. Heitler and F. London, *Z. Physik*, 1927, **44**, 455; *A.*, 1927, 923; F. London, *ibid.*, 1928, **46**, 455; *A.*, 1928, 344; W. Heitler, *Physikal. Z.*, 1930, **31**, 185; *A.*, 525; F. London, *Naturwiss.*, 1930, **17**, 516.

* This phenomenon is so essential to the theory that, although it is an old one, there may be some utility in explaining it briefly here. Suppose, for example, we have two equal pendulums in resonance. If they were not in resonance, their motions could be represented by the equations, $-d^2x/dt^2 = a^2x$, and $-d^2y/dt^2 = a^2y$, x and y being the respective displacements and a a constant. When they are isolated the frequency of each is $a/2\pi$. When they are in resonance each transmits a certain force to the other, and its own motion is modified by the reaction. The equations become $-d^2x/dt^2 = a^2x + b^2y$ and $-d^2y/dt^2 = a^2y + b^2x$. If we write $x = A \sin pt$ and $y = A \sin (pt + \epsilon)$, substitute in the differential equations, and solve for p, we find *two* values: one of these gives a frequency greater than the undisturbed frequency, $a/2\pi$, and the other gives a smaller frequency. The corresponding values of ϵ are 0 and π. If the *phases* of the two pendulums are identical or exactly opposed the pendulums vibrate jointly with the one or the other permissible frequency. For any other relation of the phases, both frequencies co-exist and give rise to beats in such a way that when the amplitude of one pendulum is a maximum that of the other is zero. The energy flows backwards and forwards from one to the other in a remarkable manner as may easily be shown experimentally. (Something analogous to this is what the quantum physicists mean, when they talk about an "exchange" of electrons between two atoms.)

The stability of molecules can in principle be investigated. The perturbation of ψ by the mutual interaction of the two atoms is what causes the splitting of the possible energy levels into two sets, the lower of which is permitted by the Pauli principle when the electrons have opposite spins. Since this perturbation is the greater the nearer the atoms approach, the energy is smaller, *i.e.*, the attraction greater. But eventually nuclear repulsion predominates and thus the total energy passes through a minimum for a certain nuclear distance. This is the equilibrium position of the two atoms in the molecule. It need hardly be said that the actual calculation is almost impossible except in very simple or idealised examples.

A systematic investigation of the symmetry relationships of atoms with different numbers of electrons in quantum mechanical resonance, in conjunction with the Pauli principle, gives most of the known facts about chemical valency in a qualitatively correct manner.[9] The 1, 3, 5, 7 valencies of the halogens, and the 2, 4, 6 valencies of the oxygen group, and the restriction of the valencies of fluorine to one are, for example, explained. It must not be forgotten that the restriction of the possibility of combination to those cases which are in accordance with the rules of chemical valency depends entirely on the application of Pauli's principle and is *not* contained in the quantum mechanical equations. The principle itself is in one sense just as empirical and not much more fundamental than the rules of valency which chemistry had already established. But the great advance is that the facts of chemistry are brought into striking relation with those of spectroscopy. The connexion is crystallised in the statement that the chemical valency is one less than the spectral multiplicity.

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[9] Compare ref. 8; also M. Born, *Z. Physik*, 1930, **64**, 729.

Two atoms which could not combine in their normal state may combine in unexpected ways if one of them is optically excited, since the excitation changes the quantum numbers and thus may destroy a symmetry which in the unexcited state led to chemical saturation. This explains certain spectra attributable to otherwise unknown compounds.

Quantum mechanical resonance is important in several other ways. The splitting of a single frequency into two explains the two non-combining spectral series of helium (ortho- and para-helium) and other similar spectroscopic facts. It is also possible that resonance effects have something to do with the occasional transference of energy between atoms and molecules at distances considerably greater than the " collision " diameter of the kinetic theory. For example, the quenching of fluorescence of gases by other gases appears occasionally to be so strong that there would not have been time for normal collisions during the life of the optically excited atom or molecule : this is expressed by saying that the deactivating collisions occur with a large " collision area." [10]

The chemical forces which were referred to above were naturally of the so-called homopolar kind. The treatment of the polar forces acting between ions in lattices is less characteristically quantum mechanical and will not be discussed here. Reference should be made, however, to the work of J. E. Lennard-Jones and his collaborators, which has thrown much additional light on the properties of ionic lattices in recent years.[11] The transition from non-polar to polar linking is discussed by R. Samuel and L. Lorentz.[11a]

R. Eisenschitz and F. London [12] have recently elaborated the quantum-mechanical treatment of the interaction of two atoms, in such a way as to give the original theory of the homopolar bond as a first approximation and to include a treatment of the so-called van der Waals forces. The two existing theories of these forces are those of W. H. Keesom [13] and P. Debye.[14] The former is based on the electrostatic action of rigid dipoles or quadrupoles, the latter

[10] *Ann. Reports*, 1927, **24**, 327, ref. 50; W. P. Baxter, *J. Amer. Chem. Soc.*, 1930, **52**, 3920; H. Kallmann and F. London, *Z. physikal. Chem*, 1929, [*B*], **2**, 207; *A.*, 1929, 487.

[11] Compare J. E. Lennard-Jones and (Miss) B. M. Dent, *Proc. Roy. Soc.*, 1928, [*A*], **121**, 247; *A.*, 1929, 17.

[11a] *Z. Physik*, 1929, **59**, 53; *A.*, 1930, 137.

[12] *Z. Physik*, 1930, **60**, 491; *A.*, 525; F. London, *ibid.*, 1930, **63**, 245; *A.*, 1239.

[13] *Physikal. Z.*, 1921, **22**, 129.

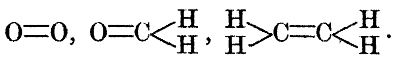
[14] *Ibid.*, 1920, **21**, 178; 1921, **22**, 302; *A.*, 1920, ii, 356.

on the modification of existing dipoles by induction. In Keesom's theory, the force diminishes rapidly with increasing temperature, since with increasing velocity there is less time for orientation into the position of attraction. In Debye's theory, there is a term independent of temperature. Both theories have to proceed in a semi-empirical manner and derive the electric moments from the known van der Waals forces : in particular, a quadrupole moment has to be assumed for the inert gases, which is not consistent with the spherical symmetry which these gases possess in the wave-mechanical theory. The wave-mechanical model of hydrogen gives a quadrupole moment which in Debye's or Keesom's theory would have led to far too small a value of van der Waals's constant *a*. The quantum-mechanical problem can only be treated in a very general way but appears to give results of the right order of magnitude : the principle is to take into account the mutual perturbations of the periodic electronic motions. The chemical valency forces are accounted for by resonance and the Pauli principle, appear in the first approximation, and have a very short range : the van der Waals forces appear when the equations are solved to the second approximation, and diminish with distance much less rapidly.

Another method of calculation used by J. E. Lennard-Jones [15] gives the right order of magnitude for the attraction between two hydrogen atoms and agrees with Eisenschitz and London.

G. Gentile [16] calculates the forces between a hydrogen atom and a helium atom and between two helium atoms. The distance between two atoms in liquid helium thus found is approximately right.

From the chemical standpoint, one of the more interesting developments of the theory is the attempt by E. Hückel [17] to account for the stability of the double bond to rotation. He begins with J. E. Lennard-Jones's electronic structure of the oxygen molecule,[18] imagines then two hydrogen nuclei drawn out from the oxygen to give formaldehyde, and then the process repeated to give ethylene :



$$\mathrm{O{=}O},\quad \mathrm{O{=}C}{<}^{\mathrm{H}}_{\mathrm{H}},\quad {}^{\mathrm{H}}_{\mathrm{H}}{>}\mathrm{C{=}C}{<}^{\mathrm{H}}_{\mathrm{H}}.$$

A discussion of the Schrödinger functions and of the mutual potential energies of the electric charges leads to the conclusion that there is a minimum energy for a definite orientation of the atoms, *i.e.*, the "bond" possesses "rigidity." If the two substituents joined to each carbon atom are different, there are two stable plane arrangements (*cis* and *trans*), though the two energy minima associated with them need not be equal. The energy which must be employed in causing a rotation about the "double bond" is connected essentially with "the mutual electrostatic action of the electronic clouds of the valency electrons which bind the substituents, and the cloud of the two electrons of the double bond." The former have their maxima in the planes of the substituents, and the latter in the plane perpendicular to these. The electronic clouds interfere with one another more when rotation occurs than in the plane configuration. (The picture thus presented depends on the earlier interpretation of Schrödinger's equation, according to which electrons in orbits of low quantum number are replaced by continuous clouds of electricity : the validity of Hückel's calculations does not, of course, depend upon the admissibility of this picture, but if we wish to avail ourselves of such help as it offers, we must combine it with the statement that, although an electron is not a cloud of electricity, there are purposes for which it is convenient to regard it as one.)

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[15] *Proc. Roy. Soc.*, 1930, [*A*], **129**, 598.

[16] *Z. Physik*, 1930, **63**, 795; *A.*, 1234.

[17] *Ibid.*, 1930, **60**, 423; *A.*, 525.

[18] *Trans. Faraday Soc.*, 1929, **25**, 668; *A.*, 1929, 1360.

Turning from the consideration of " chemical " forces to electrostatic actions, it is interesting to note that a " collision " between two similar particles, exerting Coulomb forces on each other, occurs differently when classical laws are superseded by wave-mechanical laws. For example, in collisions between α-particles and helium nuclei the amount of scattering at 45° calculated by wave mechanics is twice that expected from classical theory, a result predicted by N. F. Mott,[19] and confirmed experimentally by J. Chadwick.[20]

The Elementary Processes of Chemical Change.

The discussion of chemical forces at once raises the questions, on the one hand, of the structure of molecules and of the more complex formations which they in turn build up, and on the other hand, of the elementary processes involved in the changing partnerships of atoms which constitute chemical transformation. A number of aspects of this second question will be dealt with in the present section.

The heat of activation of a chemical reaction such as $2HI = H_2 + I_2$ is less than the energy required to resolve all the linkages in the reacting molecules, and thus allow the completely free atoms to rearrange themselves into the structure of maximum stability. Resolution into atoms sometimes occurs, especially in certain reactions of the halogens. Examples are referred to in a later section. But this process must be regarded as the limiting case of the excitation of the vibrational degrees of freedom of the molecules, which is the general form of activation and only reaches the limit of dissociation in exceptional circumstances.

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[19] *Proc. Roy. Soc.*, 1930, [*A*], **126**, 259; *A.*, 269.

[20] *Ibid.*, 1930, [*A*], **128**, 114; *A.*, 1085.

The energy of activation of the reaction $AB + CD = AC + BD$ represents the sum of the energies possessed by the molecules AB and CD at the point where their atoms are stretched apart just enough to be able to rearrange themselves readily. Its value depends, therefore, on the form of the curves which represent the potential energies of the several molecules as a function of the respective nuclear separations.[20a] Attempts to correlate the heat of activation with a known dissociation energy must thus, in general, be unsuccessful. H. Eyring [21] has suggested a rule for calculating heats of activation in bimolecular reactions in terms of a tabulated series of " heats of linkages." There is too much uncertainty about the heats of linkage themselves, and too little experimental material to allow a really good test of the validity of the rule, but it is clear on general theoretical grounds that such a principle can never provide more than an empirically valuable approximation.

D. S. Villars,[22] following a more generalised discussion of R. M. Langer,[23] approaches the matter in a more fundamental way by considering the reaction $2HI = H_2 + I_2$ in relation to the potential energy curves of the molecules H_2, I_2 and HI. A fairly good idea of the variation in potential energy with the separation of the atoms in a diatomic molecule can be obtained from the band spectrum and plotted in the form of a curve. The hypothesis is now made that two atoms in different molecules can " change allegiance " readily when the nuclear separations of the two reacting molecules, here the two hydrogen iodide molecules, are such that they can give rise to two of the molecules, H_2 and I_2, with the same total energy content as themselves, and with no change of the various nuclear separations in the process. This condition is analogous to one which Franck and Condon have found to hold in the transitions which spectroscopy reveals. In the example considered, the equation expressing the condition has naturally an infinite number of solutions, a very large number of which Villars tabulates by trial measurements on the potential-energy curves. But, of all the solutions, there is none in which the sum of the initial energies of the two hydrogen iodide molecules is less than an amount of the order of magnitude of the observed heat of activation.

[20a] H. Kallmann and F. London, *Z. physikal. Chem.*, 1929, [*B*], **2**, 207; *A*., 1929, 487.

[21] *Ibid.*, 1930, [*B*], **7**, 244; *A*., 546.

[22] *J. Amer. Chem. Soc.*, 1930, **52**, 1733; *A*., 832.

[23] *Physical Rev.*, 1929, [ii], **34**, 92; *A*., 1929, 983.

If this picture of the process of activation be a true one, it gives a great chemical importance to Franck's principle.[24] It may be remarked here that the existence of an energy of activation can be accounted for by the following qualitative statement of what is really implicit in Villars's numerical computations. The equilibrium distance between two hydrogen atoms in the hydrogen molecule is less than that between the two hydrogen atoms in two hydrogen iodide molecules colliding in such a way as to place the iodine atoms at a suitable distance for formation of an iodine molecule. According to Franck's principle, the distance between the two hydrogen nuclei must not vary during the atomic rearrangements. If, therefore, the chemical change is to take place, a hydrogen molecule with a considerable potential energy of atomic separation must be produced. This can only happen if the original hydrogen iodide molecules were activated to a degree sufficient to provide this energy. The idea contained in Villars's paper is elaborated by J. Franck and E. Rabinowitsch [25] to a rule, *viz.*, that the heats of activation of bimolecular reactions must be greater the smaller the ratio of the nuclear distances of the molecules involved to the molecular radii, which give the distance of nearest approach in collision. This principle, as they point out, leads to very small heats of activation for reactions between such molecules as those of chlorine and iodine, very high ones for reactions between such molecules as hydrogen, nitrogen, and oxygen, and intermediate values where hydrogen reacts for example with iodine.

Something like the above seems very probably to represent the true nature of activation : the energy of activation can thus be calculated only when the potential-energy curves are known, as well as some condition determining the point at which rearrangement takes place.[26] Many attempts are made to analyse the mechanism of reactions by resolving them into stages involving the initial production of free atoms or radicals, and the subsequent interaction of these with other molecules : (*a*) $AB = A + B$, (*b*) $A + CD = AC + D$, and so on. According to observations of M. Polanyi and others [27] on reactions of the type $Na + Cl_2 = NaCl + Cl$, which occur in flames, every collision between a free atom and a molecule is successful, *i.e.*, no activation is needed, as long as the change is exothermic. In these circumstances, the total heat of activation of a complex reaction can be determined in terms of heats of linkage. For example, H. J. Schumacher,[28] discussing the experimental data of M. J. Polissar,[29] on the reaction $CH_2I{\cdot}CH_2I \longrightarrow CH_2{:}CH_2 + I_2$ in carbon tetrachloride solution, postulates $CH_2I{\cdot}CH_2 -$ as an intermediate, and with the aid of various assumptions deduces the energy of the C—I link and the energy difference between the C—C and the C=C link. Although there is much direct evidence that free atoms and radicals play their part in halogen reactions, yet such assumptions in other cases ought not to be made unless justified by some direct positive evidence.

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[24] See this Report, p. 22. [25] *Z. Elektrochem.*, 1930, **36**, 794; *A.*, 1378.

[26] Compare also A. Ölander, *Z. physikal. Chem.*, 1930, [*B*], **7**, 311.

[27] *Ibid.*, 1928, [*B*], **1**, 3, 21, 30; *A.*, 1928, 491.

[28] *J. Amer. Chem. Soc.*, 1930, **52**, 3132; *A.*, 1255.

In connexion with the above, it must be noticed that the principle of Polanyi mentioned, although a valuable and interesting generalisation, is not absolute, and that according to G. B. Kistiakowsky [30] the fraction of successful collisions in the reactions $Cl + H_2 = HCl + H$ and $O + H_2 = H + OH$ is less than 10^{-3}.

While rejecting the assumption that energies of activation can in general be expressed in terms of heats of linkage alone, it is quite possible to concede a certain general parallelism in the sense that the tighter the binding of the atoms in a molecule the higher will be the heat of activation for reactions in which that molecule takes part. Thus, for certain purposes of qualitative comparison we may be able to make use of a knowledge of binding energies. R. Mecke [31] considers a series of simple chemical reactions involving molecules such as CO_2, H_2O, N_2O, and so on, tabulates dissociation energies obtained from spectroscopic data, assumes that the reactions occur by way of free atoms and radicals, and uses the principle that that atom splits off most readily which has the smallest energy of dissociation. By considering the relative probability of processes such as $CO_2 = C + O_2$ and $CO_2 = CO + O$, he draws a general picture of reaction possibilities which is in harmony with chemical facts. This, however, hardly proves that free atoms and radicals participate in the actual processes which occur.

Molecular Spectra and Chemical Change.

As a method for investigating the elementary processes of chemical change, the study of the relation between molecular spectra and chemical, or more particularly photochemical, behaviour is receiving much attention.[32] Molecules give band spectra,[33] the general position of a band system in the whole spectrum being determined by the electronic energy, the separate bands of a group corresponding

[29] *J. Amer. Chem. Soc.*, 1930, **52**, 956; *A.*, 548.

[30] *Ibid.*, p. 1868; *A.*, 871.

[31] *Z. physikal. Chem.*, 1930, [*B*], **7**, 108.

[32] Compare the report by H. S. Taylor, *J. Physical Chem.*, 1930, **34**, 2049.

[33] See, *e.g.*, R. Mecke, "Bandenspektra und ihre Bedeutung für die Chemie," Berlin, 1929; and S. Barratt, *Ann. Reports*, 1926, **23**, 297.

to different numbers of vibrational quanta, and the fine structure of the bands depending on the varying numbers of rotational quanta. Sometimes the band system is succeeded on the short-wave side by a continuous spectrum, the disappearance of vibrational quantisation indicating that the molecule is resolved into atoms. By comparing the energy corresponding to the frequency where the continuum begins with the thermally-determined dissociation energy, it has been found that a homopolar diatomic molecule is usually resolved into one normal atom and one atom in an electronically excited state. If the optical states of the atom are known independently, the thermal energy of dissociation can conversely be estimated.[33a]

If the frequency of the active light in a photochemical reaction is known, we can tell from the nature of the spectrum in this region whether the primary photochemical process has produced free atoms or an activated molecule.

The relation of continuous spectrum to band spectrum is not always quite as simple as that just described. The alkyl halides, for example, give bands at shorter wave-lengths and a continuous spectrum at longer wave-lengths.[34] This can be explained by supposing that there exist two different *electronic* states of the molecule the dissociation limits of which are different. In the higher electronic state, the energy of the molecule is greater than would correspond to dissociation had the molecule been in the lower electronic state. Thus a spontaneous transformation is possible, involving an electronic change and simultaneous dissociation. Now, it is possible also that this spontaneous transformation from the discrete (band) region of the higher electronic level to the continuum of the lower does not occur when the molecule has a large number of vibrational quanta, but does occur when it has a small number. This state of affairs can arise when there is an appropriate relation between the potential energy–displacement curves for the vibrating molecules in the two electronic states,[35] and is accounted for by the Franck principle already referred to. This principle, which is founded on a study of intensity relationships in band spectra, asserts that electronic changes in a molecule only occur in such a way that the accompanying change in nuclear distance and relative velocity of the two atoms is small. In the present example, the change in nuclear distance accompanying the change from the higher (undissociated) to the lower (dissociated) electronic state would be too great in the higher vibrational states. Hence these are stable. In the lower vibrational states the change in distance is not too great and transformation occurs, followed immediately by dissociation.

[33a] Compare R. T. Birge, *Trans. Faraday Soc.*, 1929, **25**, 707; *A.*, 1930, 3.

[34] G. Herzberg and G. Scheibe, *Z. physikal. Chem.*, 1930, [*B*], **7**, 390.

[35] G. Herzberg, *Z. Physik*, 1930, **61**, 604; *A.*, 831; J. Franck and H. Sponer, *Nach. Ges. Wiss. Göttingen*, 1928, 241.

The phenomenon known as "pre-dissociation" is explicable in a similar way. Some years ago, V. Henri discovered that, with decreasing wave-length, but before the region of continuous absorption is reached, the rotational fine structure of bands sometimes disappears, the bands themselves remaining quite distinct. It is now known that the fine structure may sometimes reappear at still shorter wave-lengths. The appearance of the diffuse structureless bands means that the rotations cease to be quantised while the vibrations still remain quantised. This depends upon the fact that after absorption of the light there is a redistribution of the various kinds of energy in the molecule, which occurs during a period small compared with the time of rotation, but long compared with the time of vibration.[36] It probably involves the actual dissociation of the molecule.[37] Bonhoeffer and Farkas showed that considerable photochemical decomposition of ammonia did indeed occur in the region of diffuse bands. Many substances show pre-dissociation, including nitrogen peroxide, sulphur vapour, benzaldehyde, acetaldehyde, and other aldehydes. The existence of two frequency limits, above and below which pre-dissociation does not appear, can be explained by Franck's principle in a manner analogous to the explanation given above of the long wave-length continuum of the alkyl halides—with small frequencies the energy is not great enough for dissociation, while with frequencies above the higher limit the change in nuclear separations involved in the transformation to the dissociable state would be too great.

Some progress is being made towards correlating the existence of pre-dissociation with photochemical behaviour. With aldehydes, for example, Henri suggested that absorption of light in the pre-dissociation region leads to decomposition, while absorption of light in the region of normal band absorption gives rise to activated molecules which tend to polymerise rather than to decompose. M. de Hemptinne[38] obtained experimental evidence in support of this point of view in the case of benzaldehyde. On the other hand, G. B. Kistiakowsky,[39] studying the photochemical decomposition of nitrosyl chloride, in which two molecules are transformed for each quantum absorbed, finds that the mechanism probably consists

[36] M. Born and J. Franck, *Z. Physik*, 1925, **31**, 411; *A.*, 1925, ii, 266.

[37] K. F. Bonhoeffer and L. Farkas, *Z. physikal. Chem.*, 1927, **134**, 337.

[38] *J. Phys. Radium*, 1928, **9**, 357.

[39] *J. Amer. Chem. Soc.*, 1930, **52**, 102; *A.*, 306.

in an excited molecule colliding with a second molecule. The quantum of the active light is smaller than the heat of dissociation (thermally measured), and the band spectrum possesses rotational fine structure, showing that " pre-dissociation " is not a necessary state for chemical activation. As with thermal reactions, the distinction between activation and dissociation is maintained.

This is a suitable place in which to refer to the very interesting work of R. G. W. Norrish[40] on the photochemical equilibrium $2NO_2 \underset{\text{dark}}{\overset{\text{light}}{\rightleftharpoons}} 2NO + O_2$. The reaction is of great interest in that there exists a true " photochemical threshold " in the middle of the absorption region. In other examples, apparent critical wave-lengths at which the photochemical change first becomes appreciable proved to be illusory and due to a rapid fall in the actual absorption in the vicinity of the supposed threshold wave-length.[41] R. G. Dickinson and W. P. Baxter,[42] however, observed such a limit for the nitrogen peroxide dissociation in the region where no fall in absorption occurred, and Norrish showed that the limit was quite a sharp one, the quantum efficiency at 436 μμ being zero and that at 405 μμ being 0·74, rising to 2 at shorter wave-lengths. The absorption is high and shows fine structure. V. Henri[43] reports that pre-dissociation sets in between 370 and 380 μμ (there being also a second limit between 245·9 and 220·0 μμ). Thus Norrish suggests that the primary process is not dissociation of NO_2 into $NO + O$ but a collision between an excited NO_2 molecule and a normal one. It is also important to note that, when light of greater wave-length than the threshold value is absorbed, it is emitted again as a fluorescence which has been detected experimentally by Norrish and further studied by W. P. Baxter[44] (who, incidentally, finds a number of interesting results on the quenching of the fluorescence by foreign gases). Baxter, however, thinks the collision mechanism unlikely, since the quantum efficiency at 405 μμ is not diminished by addition of carbon dioxide, nor by lowering the pressure to 0·01 mm.

A problem allied to those discussed above, namely, that of the rotational states of molecules produced by chemical reaction, is treated by H. Beutler and E. Rabinowitsch.[45] Considering " elementary " reactions of the types $A + BC = AB + C$ and

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[40] *J.*, 1927, 761; 1929, 1158, 1604, 1611; *A.*, 1927, 528; 1929, 893, 1022.

[41] E. J. Bowen, *Trans. Faraday Soc.*, 1926, **21**, 543.

[42] *J. Amer. Chem. Soc.*, 1928, **50**, 774; *A.*, 1928, 491.

[43] *Nature*, 1930, **125**, 202; *A.*, 272.

[44] *J. Amer. Chem. Soc.*, 1930, **52**, 3920; *A.*, 1500.

[45] *Z. physikal. Chem.*, 1930, [*B*], **8**, 231; *A.*, 975.

$A + B = AB$, they work out the relations which must hold, according to the quantum laws and the various mechanical conservation laws, between the energy liberated in the reaction, the effective " collision area " of the reacting molecules, and the rotational state of the products. The results can be applied in an interesting, if speculative, way to the interpretation of the experiments of E. Gaviola and R. W. Wood,[46] who had found that in the fluorescence light from a mixture of mercury and water vapour, the HgH bands emitted have a distribution of intensity corresponding to a predominance of small rotational quanta; while in the HgH bands from a mixture of mercury, hydrogen, and nitrogen, the higher rotational states predominate. Modifying the original explanation of Gaviola and Wood for various reasons, Beutler and Rabinowitsch suggest that the processes occurring are as follows :

(1) $Hg' + H_2 = HgH + H$ (exothermic),
(2) $Hg' + H_2O = HgH + OH$ (slightly endothermic),
(3) $HgH + Hg' = HgH' + Hg$,
(4) $HgH' = HgH +$ light.

The dashes signify optically excited states. Reaction (1), there is reason to suppose from the influence of hydrogen in quenching mercury fluorescence, takes place as though the " collision area " were considerably greater than the normal kinetic theory value.[47] Thus, in collision, there can be a large turning moment, and molecules in high rotational states can be produced. On the other hand, reaction (2) appears to occur only at one collision in 3000; plausibly, therefore, we can assume that the collision area is no greater than the normal one. Thus the turning moment is small and low rotational quantum states result. The last step in the argument is certainly not entirely convincing, but the investigation is a good example of the way in which attempts are being made to bring spectroscopic evidence to bear on chemical problems.

The Probability of Spontaneous Molecular Transformation.

In a unimolecular chemical reaction the current view is that there is a supply of activated molecules, maintained by collision, and that there is a definite probability that a given molecule will undergo transformation before losing its energy.[48] This probability may or may not be a continuous function of the excess of energy possessed by the molecule over the minimum required for " activation." It may in principle—and especially according to quantum-mechanical theories—even be a continuous function of the energy content over the whole range of values, with no sharp threshold of activation. But according to all theories the vast *majority* of the molecules which are transformed possess energies in a narrow range in the neighbourhood of the energy of activation. The probability of transition of these molecules is found experimentally to be such that the time elapsing between activation, " classically " regarded, and transformation is of the same order of magnitude as the period of revolution of an electron in its orbit. M. Polanyi and E. Wigner [49] arrived at this same numerical value by a theory based upon the interference of elastic waves in the molecule leading to a concentration of energy at a particular point. More recently, attempts have been made to treat the problem by the application of quantum-mechanical considerations. The results are not very definite, but the principles involved are extremely interesting.

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[46] *Phil. Mag.*, 1928, **6**, 1191; *A.*, 1929, 239.
[47] Compare refs. 10 and 44.
[48] See *Ann. Reports*, 1927, **24**, Section on " Chemical Kinetics."

All the attempts are adaptations of the Gamow theory [50] of radioactive disintegration, or of the wave-mechanical theory of " radiationless transfers " of electrons.[51] It is first necessary to explain these two theories sufficiently to show the chemical analogies. First, with regard to the question of nuclear disintegration, inside an atomic nucleus an α-particle must be under the influence of an attractive force, since nuclei in general are in fact stable. Outside the nucleus it suffers a repulsion, which is in accordance with Coulomb's law when the distance from the centre of the nucleus is greater than about 10^{-12} cm. Yet, after escaping from a nucleus, the α-particle is found not to possess the kinetic energy which it should if the repulsive forces had acted on it from the point where they begin to be effective. This is expressed by saying that the α-particles " leak through " the potential barrier surrounding the nucleus. In the wave-mechanical treatment of the matter, we take a rather idealised form of potential barrier, and write down the equations expressing the amplitude of the wave function (the square of whose absolute magnitude gives the relative number of α-particles in an element of volume) for three regions, *viz.*, inside the nucleus, in the barrier itself, and outside the nucleus. These equations involve the potential energy of the particle in the various regions. Then in a way somewhat analogous to Fresnel's treatment of reflexion and refraction of light,[52] the condition is written down that the wave function and its differential coefficient shall be continuous at the two boundaries. In this way we find the amplitude of the wave outside the nucleus, which determines the probability of escape of the α-particle. It must be remarked that the wave-mechanical treatment does not explain *why* an α-particle can escape from a region which it could not possibly leave in a "classical" manner: being a statistical method of calculation using continuous equations, it automatically provides for a certain concentration of α-particles outside the nucleus and then determines a value for this concentration. The important success of the theory is that it gives the Geiger–Nuttall law for the relation between the energy of the particle and its rate of escape, and moreover, with the numerical coefficients approximately correct.*

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[49] *Z. physikal. Chem.*, 1928, **139**, 439; *A.*, 1929, 404.

[50] G. Gamow, *Z. Physik*, 1928, **51**, 204; *A.*, 1929, 7.

[51] G. Wentzel, *Physikal. Z.*, 1928, **29**, 321; *Z. Physik*, 1927, **43**, 524; *A.*, 1927, 807.

[52] Compare, *e.g.*, Preston's " Light."

If we are prepared to admit that the transformation of an activated molecule is analogous to the disintegration of a nucleus, an analogous treatment becomes possible.[53] The actual probability of transformation cannot be satisfactorily estimated, but the interesting possibility arises that, just as those radioactive changes occur most rapidly which give α-particles of the greatest energy, so those unimolecular reactions which are most exothermic should have the greatest values of the constant B in the equation $k = Be^{-E/RT}$.

But there is no particularly good ground for assuming that the chemical changes of an activated molecule are really at all similar to a radioactive decay. The analogy of a "radiationless transfer" of an electronic system to a state of equal energy is perhaps closer. To understand the wave mechanics of this we must again rid our minds of the idea that we are giving individual attention to any member of an assemblage: the equations refer to the assemblage itself. Suppose, for simplicity, that we have a molecule AB capable of splitting up into A and B. Before and after the transformation the parts A and B can be thought of as possessing definite total energies. If letters with dashes refer to the final state, $E_A + E_B =$

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* The classical and wave-mechanical treatments may be compared with the aid of an analogy. If a large number of men stood before a wall which many could nearly but none quite jump, classical mechanics would allow none over, but wave mechanics would let a few over, the proportion being smaller the more the wall was beyond the reach of the individuals classically considered. The result is inherent in the use of the equations which only deal with assemblages. If it is asked *why* even a small proportion of classically impossible things occur, the only answer is that the question has no meaning. This answer fails to satisfy many people; whether because their habit of mind is too fixed, or because the answer is an evasive one, time must show.

[53] S. Roginsky and L. Rosenkewitsch, *Z. physikal. Chem.*, 1930, [*B*], **10**, 47; *A.*, 1377; where references to the work of Bourgin, Oppenheimer, and Langer are also given. Compare also remarks by O. K. Rice, *Physical Rev.*, 1929, [ii], **34**, 1451.

$E_{A'} + E_{B'}$. Now consider an assemblage of AB molecules. Its behaviour is described by a wave function with a frequency obtained by dividing $E_A + E_B$ by h. The assemblage of transformed molecules has a wave function with the same frequency (by the conservation of energy). Thus, even if the amplitude of its wave function is initially zero, it will grow by *resonance*.[54] The rate of change of amplitude determines the probability of the individual transformations. Such a treatment has been successfully applied to the Auger effect (transfer of an electron to a new orbit with simultaneous ejection from the atom of a second electron). In their application of the method to a chemical reaction, Roginsky and Rosenkewitsch deduce as a positive consequence that, in the equation $k = Be^{-E/RT}$, the logarithm of the constant B should be proportional to $(Q - E)/\sqrt{E}$, where Q is the heat of reaction. (The signs are such that the absolute values of Q and E are added for exothermic reactions.) This result is similar to that inferred from the assumed applicability of some analogue of the Geiger–Nuttall law to chemical reactions.

The experimental evidence is very doubtful. Unimolecular reactions of sufficiently varied heat of reaction are scarcely known. Roginsky and Rosenkewitsch consider the general balance of evidence in favour of such a relation, but their analysis is not very convincing.* The real need is for more suitable examples by which to test the relation. This is always the difficulty.

Problems of Structure.

We now turn from dynamical problems to questions of structure. One of the most direct ways of obtaining information about the configuration of simple molecules is the careful analysis of infra-red spectra [55] or of the fine structure of visible and ultra-violet band spectra. The magnitudes which can be directly inferred from such measurements are the principal moments of inertia of the molecule. When these are known, models giving the distances between the various atoms can be devised to fit them. The value of the dipole moment of the molecule serves as a useful independent control. A perfectly symmetrical molecule has all three principal moments of inertia equal; a molecule like ammonia, which has a regular pyramidal structure with the nitrogen at the apex, has two of the three moments equal; and a molecule like that of water has three different values.

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* For example, in Fig. 5 of their paper, referring to unimolecular gas reactions, there are 8 points, through which two straight lines are drawn. The point relating to Dienger's reaction should not be included, since the reaction is almost certainly not a homogeneous change at all. When this is omitted the remaining points appear almost randomly grouped about a mean.

[54] Perhaps the clearest treatment of quantum-mechanical transitions as a case of resonance between wave functions is that of E. Schrödinger, *Ann. Physik*, 1927, [iv], 83, 956.

[55] Compare C. Schaeffer and F. Matossi, "Das Ultrarote Spektrum," Berlin, 1930; R. Mecke, *Z. Elektrochem.*, 1930, 36, 589; *A.*, 1343.

According to the theory of spectra, the frequency of a line is given by $h\nu = \Delta E_{\mathrm{el.}} + \Delta E_{\mathrm{vib.}} + \Delta E_{\mathrm{rot.}}$ where $\Delta E_{\mathrm{el.}}$, etc., represent the changes in electronic, vibrational, and rotational energy accompanying the "quantum jump." Since the moments of inertia determine the rotational quanta, they are found from the $\Delta E_{\mathrm{rot.}}$ terms. In the simplest case, a quantum jump from the *m*th to the $(m - 1)$th rotational state is represented by a frequency $\nu_{\mathrm{rot.}} = mh/4\pi^2 A$. The moment of inertia, A, can be found from the spacing of the pure rotation bands in the long infra-red, from the spacing of the rotational fine structure of the vibration bands in the short infra-red, from the distance between the maxima of intensity in the P and R branches of an infra-red double band, and also from the fine structure of the electronic band spectra. Not all methods are always applicable. In an infra-red rotation vibration spectrum, the P and R branches represent respectively the parts of the band where the rotation quantum is deducted from or added to the vibrational energy. The presence or absence of a Q-branch is significant: this branch represents the pure change in vibrational energy without an accompanying change of rotational state, and is nearly always absent from the infra-red spectra of diatomic gases.

The number of fundamental frequencies occurring in the infra-red vibration spectrum is also an important matter, though not always an easy one to settle. It is closely connected with the structure of the molecule: for example, if methane has the tetrahedral form it should possess four, a triatomic non-linear molecule in general has three, whilst a diatomic molecule has one only. A vibration in which the electric moment of the molecule does not change gives rise to no infra-red absorption band, but can combine with another frequency and appear, for example, in the Raman effect.[56] Two of the four theoretical frequencies of the tetrahedral methane model would be inactive in this sense.

In the light of these general considerations, some of the recent work can be summarised. C. R. Bailey [57] discusses afresh the question of the water molecule, previously treated by Eucken, Hund, Mecke, and others. The essential facts are that the infra-red spectrum gives three values for the moments of inertia, and requires two fundamental frequencies for its interpretation (two of the three theoretical frequencies are equal, or one is inactive). All models are variants of a triangular one. Bailey favours an isosceles triangle, the equal sides of which are 1·07 × 10^{-8} cm. and the included angle 64°. Eucken's model gave 1·03 × 10^{-8} cm. and 110° 56′, Hund's 1·04 × 10^{-8} cm. and 64°, and Mecke's 0·86 × 10^{-8} cm. and 96°. F. I. G. Rawlins,[58] discussing the carbon dioxide molecule, decides in favour of the accepted linear form. Further work has been done on the spectrum of ammonia : [59] all the infra-red bands are stated to be derivable from three fundamental frequencies. Badger and Mecke find three moments of inertia, of which two are nearly equal (2·74 and 2·79 × 10^{-40} C.G.S. units respectively)—complete symmetry of the pyramidal structure would require two to be exactly equal. These authors estimate the height of the pyramid to be 0·517 × 10^{-8} cm. and the distance between the hydrogen atoms to be 1·43 × 10^{-8} cm., neglecting the slight asymmetry indicated by the imperfect equality of two moments of inertia.

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[56] See *Ann. Reports*, 1929.

[57] *Trans. Faraday Soc.*, 1930, **26**, 203; *A.*, 661.

C. P. Snow and E. K. Rideal [60] find that the overtone of the previously investigated nitric oxide band has a Q-branch like the fundamental, but unlike most diatomic molecules. The anomaly is connected with the presence in the nitric oxide molecule of an odd number of electrons, the existence of the electron impulse removing the prohibition of an $m \longrightarrow m$ transition. C. P. Snow [61] has investigated nitrous oxide and suggests a linear structure similar to that of carbon dioxide and carbon disulphide.[61a] Attention has also been given to the infra-red properties of ozone,[62] benzene and its halogen derivatives,[63] and acetylene.[64] The last appears to be quasi-diatomic, with one moment of inertia, the C$\equiv$C distance being 1·19 × 10^{-8} cm.

V. Henri and his collaborators have attacked the problem of polyatomic molecules by studying the visible and ultra-violet spectra. V. Henri and S. A. Schou [65] had shown that formaldehyde has a Y-shaped molecule, the fine structure of the bands revealing a double set of rotational states. More recent work shows carbonyl chloride and thiocarbonyl chloride [66] to have structures analogous to that of formaldehyde. Among other studies of spectra may be mentioned those of chlorine,[67] chlorine monoxide,[68] and chlorine dioxide.[69]

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[58] *Trans. Faraday Soc.*, 1929, **25**, 925; *A.*, 1930, 19.

[59] R. M. Badger and R. Mecke, *Z. physikal. Chem.*, 1929, [*B*], **5**, 333; *A.*, 1929, 1363; R. M. Badger, *Physical Rev.*, 1930, [ii], **35**, 1038; J. W. Ellis, *J. Franklin Inst.*, 1929, **208**, 507; compare Robertson and Fox, *Ann. Reports*, 1928, **25**, 11.

[60] *Proc. Roy. Soc.*, 1930, [*A*], **126**, 355; *A.*, 273.

[61] *Ibid.*, 1930, [*A*], **128**, 294; *A.*, 1089.

[61a] C. R. Bailey and A. B. D. Cassie, *Nature*, 1930, **126**, 350; *A.*, 1345.

[62] O. R. Wulf, *Proc. Nat. Acad. Sci.*, 1930, **16**, 507; *A.*, 1226.

[63] J. F. Daugherty, *Physical Rev.*, 1929, [ii], **34**, 1549; *A.*, 1930, 273.

[64] K. Hedfeld and R. Mecke, *Z. Physik*, 1930, **64**, 151; *A.*, 1235; W. H. J. Childs and R. Mecke, *ibid.*, p. 162; *A.*, 1236; R. Mecke, *Z. Elektrochem.*, 1930, **36**, 803; *A.*, 1343.

[65] *Z. Physik*, 1928, **49**, 774; *A.*, 1928, 935.

A fundamentally new method of investigating the structure of molecules has been developed by Debye. It allows *X*-ray interference measurements to be carried out with molecules in the gaseous state. The diffraction effects observed in the experiments of Laue and Bragg depend upon the regular arrangement of scattering centres in a crystal lattice, and it might be supposed that with a gas the random orientation of the molecules would destroy any trace of diffraction maxima and minima. As early as 1915, however, it was calculated by P. Debye [70] and by P. Ehrenfest [71] that, if a beam of *X*-rays passes through a gas the molecules of which contain several atoms capable of exerting a scattering action, then the intensity of the scattered radiation, averaged over all possible orientations of the molecules themselves, still shows maxima and minima at definite angles. If the molecules contain atoms 1 . . . *i*, *j* . . . *n*, the scattered intensity is given by the formula [72]

$$J = \frac{1 + \cos^2\theta}{2} \sum_1^n \sum_1^n \psi_i \psi_j \frac{\sin x_{ij}}{x_{ij}}$$

θ is the angle between the primary and the scattered ray, ψ is a function representing the scattering power of the individual atoms, and $x_{ij} = \frac{4\pi}{\lambda} l_{ij} \sin\frac{\theta}{2}$, λ being the wave-length of the radiation and l_{ij} *the distance of the atom* i *from the atom* j *in the molecule.* The important term is $\sin x/x$ which gives maxima and minima with a spacing depending on l. To a first approximation, the ψ terms may be taken as constant, but a more exact treatment is given by Debye.[73]

The maxima and minima were first detected experimentally with the vapour of carbon tetrachloride.[74] The principle of the apparatus is illustrated in Fig. 1.

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[66] V. Henri and O. R. Howell, *Proc. Roy. Soc.*, 1930, [*A*], **128**, 178; *A.*, 1088.

[67] A. Elliott, *Proc. Roy. Soc.*, 1930, [*A*], **127**, 638; *A.*, 977.

[68] C. F. Goodeve and J. I. Wallace, *Trans. Faraday Soc.*, 1930, **26**, 254; *A.*, 660.

[69] C. F. Goodeve and C. P. Stein, *ibid.*, 1929, **25**, 738; *A.*, 1930, 11.

[70] *Ann. Physik*, 1915, **46**, 809.

[71] *Vers. K. Akad. Amsterdam*, 1915, **23**, 1132.

[72] P. Debye, *Proc. Physical Soc.*, 1930, **42**, 340; *A.*, 977.

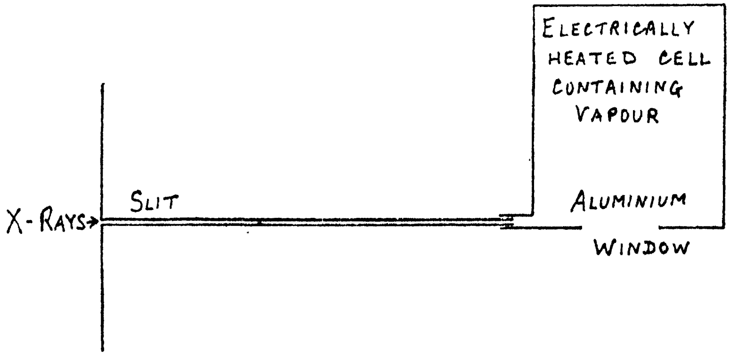
[73] *Idem*, *Physikal. Z.*, 1930, **31**, 419; *A.*, 843.

[74] P. Debye, L. Bewilogua, and F. Ehrhardt, *ibid.*, 1929, **30**, 84.

Three maxima could be observed at 36°, 65°, and 110°. The contribution of the carbon atoms to the scattered radiation is negligible; only the four chlorine atoms count. Calculation, with the appropriate corrections, gave the value $l = 2{\cdot}99 \times 10^{-8}$ cm. for the distance between any two of them.

No diffraction can be detected with oxygen and nitrogen. The maxima are faint with carbon dioxide but marked with carbon disulphide. It appears that when the atoms themselves are approximately half as big as the distance between them the effects become obscured. For the distances between the chlorine atoms in *cis*- and *trans*-dichloroethylene, the values found are respectively $3{\cdot}6$ and $4{\cdot}1 \times 10^{-8}$ cm. For ethylidene dichloride the distance is $4{\cdot}4 \times 10^{-8}$ cm.[75] It is evident that the structure of the molecule can be searchingly investigated by this new method. Analogous results have been found by R. Wierl [76] for the scattering by carbon tetrachloride and other substances, not of *X*-rays, but of fast-moving electrons.

Fig. 1.



After the study of simple isolated molecules, the natural transition is to that of their aggregation to form liquids and solids. Attempts have been made by Debye and H. Menke [77] to disentangle the intermolecular from the intramolecular part of the *X*-ray interferences from liquids, and promise to throw light on the obscure question of the true structure of liquids, but are hardly ripe for report yet. It appears, however, that in mercury certain distances of the atoms from one another are favoured at the expense of others in a " quasi-crystalline " way. With regard to solids, the *X*-ray analysis of crystal structure is being systematically extended to every conceivable type of substance; the theory of ionic lattices, originally attacked by Born, is gradually being developed with help from quantum mechanics and from the infra-red investigation of ionic crystals; and progress is being made with the theory of metals. These matters must unfortunately be passed over here with this mere reference. A few details may, however, be singled out for consideration.

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[75] P. Debye, *Physikal. Z.*, 1930, **31**, 142; *A.*, 400.

[76] *Ibid.*, p. 366; *A.*, 652.

[77] *Ibid.*, p. 797; *A.*, 1350.

Much attention has been given in the last few years to the *X*-ray analysis of compounds, such as cellulose and its derivatives, which possess a fibrous structure resulting from an orientation of " crystallites " or " micelles " parallel to one particular axis. These substances are interesting as a transition from simple molecules and structures towards the complex organisations adapted to the functions of life. The method of investigation [78] is essentially to examine the *X*-ray diagrams obtained under two sets of conditions. When the rays fall on the material in the direction of the fibre axis, a Debye–Scherrer pattern is obtained, because the micelles or microcrystals may have all possible orientations except for the direction of their long axes; when, however, the rays are incident perpendicular to the axis of the fibres, a different type of pattern is obtained, since the long axes are parallel to the fibres (fibre diagram).

By applying this method of analysis, the changes occurring in cellulose under the action of chemical reagents on various physical treatments can be investigated. Most of the work is too specialised to summarise, but may be exemplified by that of K. R. Andress,[79] who concludes that the change occurring during the " mercerisation " of natural cellulose is the rearrangement of the main chains to more stable relative positions. H. Mark and K. H. Meyer [80] distinguish two kinds of reaction of cellulose, " micellar surface reactions " and " permutoid " reactions. In the first kind, the reagent penetrates between the micelles without attacking their internal structure; the orientation may, however, be disturbed and the " fibre " diagram changes to a Debye–Scherrer diagram. In the second kind of reaction, the reagent penetrates the whole structure, attacking specific chemical groupings at each point of the lattice.

Although they relate to a different type of structure, it is interesting to mention some measurements made by A. Müller.[81] He has found that while the short axes of long-chain normal paraffins change on the average by 6·8% and 1·9% respectively between the temperature of liquid air and the melting point, the change in the long axis is too small to measure. This indicates that the end groups of the molecules move apart, but that the length of the chain probably does not alter with increasing temperature.

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[78] For list of references see (Sir) W. H. Bragg, *Nature*, 1930, **125**, 634.

[79] *Z. physikal. Chem.*, 1929, [*B*], **4**, 190; *A.*, 1930, 280.

[80] *Ibid.*, **2**, 115; *A.*, 1929, 245.

[81] *Proc. Roy. Soc.*, 1930, [*A*], **127**, 417; *A.*, 844.

In the region of more complex systems, the investigations of T. Svedberg,[82] by means of the ultra-centrifuge, on the dispersity of protein solutions have now yielded an interesting picture. There are " monodisperse " systems (*i.e.*, of homogeneous molecular weight) such as hæmoglobin and egg-albumin solutions, the former of which contains particles of molecular weight 68,000 with four iron atoms; and there are " polydisperse " systems, including gelatin and casein, the particles of which vary and are in a labile condition. Hæmocyanins, which are monodisperse, have " molecular weights " of several millions.

Surface Chemistry.

From the work of Rayleigh, Pockels, Devaux, Langmuir, and Adam, it has emerged that the unimolecular films formed by the spreading on water of insoluble substances, such as compounds with long hydrocarbon chains and an active end group, form a state of matter, the properties of which may be interpreted by an adaptation to two dimensions of the ordinary three-dimensional kinetic theory.[83] The normal method of investigating the properties of these films is to plot the " surface pressure," F, *i.e.*, the number of dynes per cm. applied to a barrier compressing the film, against the area, A, of the film. Gaseous films, condensed films, and an intermediate type which Adam calls " expanded films " are found. In the gaseous film there is free motion of the molecules over the surface, and in favourable examples, such as the esters of dibasic acids, the value of FA for low " pressures " approaches quite closely to the value, kT, derived from the two-dimensional kinetic theory. As the pressure increases, FA passes through a minimum, following a curve analogous to Amagat's pv curves for imperfect gases. Condensed films possess very much smaller areas, even at zero compression, indicating that there is a powerful lateral adhesion between the molecules, analogous to that which keeps matter in bulk in the condensed state. The area occupied per molecule is independent of the length of the hydrocarbon chain, as long as the number of carbon atoms is greater than about twelve. The smallest area at zero compression is about 20·5 sq. Å., while the area of the base of the corresponding hydrocarbon chain in crystals is shown by X-ray measurements to be about 18·4 sq. Å. Thus, either the molecules in the film are rather less closely packed, or the chain is tilted somewhat in the film, an angle of tilt of about 27° being required to account for the approximately 10% greater base area. Some compounds require bigger areas than 20·5 sq. Å., and these areas vary under compression, indicating a rearrangement of the heads of the chain. In condensed films, allotropic changes may occur at definite transition temperatures. The most interesting phenomenon is the passage from the " gaseous " to the " condensed " state in the film : at a certain pressure, the " vapour pressure " of the condensed film, the gaseous film may collapse to the small area characteristic of the condensed state. The collapse does not occur if the temperature is above the " critical " temperature. The curves giving the relation between *F* and *A* for different temperatures form a series analogous to Andrews's well-known isothermals of carbon dioxide.

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[82] *Kolloid-Z.*, 1930, **51**, 10; *A.*, 694.

[83] Compare N. K. Adam, " Physics and Chemistry of Surfaces," Oxford, 1930.

The most recent work has dealt with the esters of fatty acids [84] and with long-chain amines.[84, 85] The lower alkyl palmitates form the normal condensed films of area 20·5 sq. Å., intermediate members of the palmitate series form " expanded films " of about 85 sq. Å., while the higher members, *e.g.*, *n*-hexadecyl palmitate, give condensed films of area 41 sq. Å. The last class clearly have double close-packed chains, corresponding to the single chains of the lowest members whose alkyl groups probably plunge into the water. The abnormal behaviour of the intermediate members is explained by a violent oscillation of the hydrocarbon chains, to which Adam attributes the existence of " expanded " films in general. (It should be noted that the area of the expanded type is still much closer to that of a condensed film than to that of a gaseous film.) Results obtained with the amines lead Lyons and Rideal to maintain their previously suggested hypothesis of the " interlocking " of chains in stable films, an hypothesis which Adam criticises adversely.

The existence of two surface phases in equilibrium with each other, which the study of films has demonstrated, has been shown by N. Semenov [86] to yield a simple theory of the rather remarkable phenomena attending the condensation of metal vapours on to surfaces. As is well known, there exists a critical temperature below which the vapour condenses on to a cold surface, but above which it is entirely reflected; at the critical temperature the degree of supersaturation of the metal vapour is already very great. The proposed explanation is as follows. The vapour is in adsorption equilibrium with a " gaseous " film on the surface : when the pressure in the film reaches the two-dimensional critical pressure a condensed film is formed, which can then act as a basis for the building up of massive metal, if the vapour pressure of the metal in bulk is greater than the surface critical pressure. Analogously, there will be a critical temperature, where the pressure in the vapour corresponding to the surface critical pressure is no longer smaller than the saturated vapour pressure.

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[84] *Idem, Proc. Roy. Soc.*, 1930, [*A*], **126**, 366, 526; *A.*, 408.

[85] C. G. Lyons and E. K. Rideal, *ibid.*, 1930, [*A*], **128**, 468; *A.*, 1110.

[86] *Z. physikal. Chem.*, 1930, [*B*], **7**, 471; *A.*, 851; compare J. Frenkel's more elaborate theory, *Ann. Reports*, 1928, **25**, 352.

The assumption of a " gaseous " surface film in this connexion implies that the adsorbed molecules can move freely over the surface of the solid. That this is possible in certain circumstances has for some time appeared probable from the work of Volmer. The idea of lateral diffusion and the conception of surface gas pressure have been used by F. J. Wilkins and A. F. H. Ward [87] in discussing the question of the variation with temperature of the maximum amount of gas which a surface can adsorb. According to the simple Langmuir theory, there is no reason why the saturation limit should vary appreciably with temperature (except in special circumstances, such as multiple point adsorption depending very much on the exact spacing of the centres). Wilkins and Ward assume, however, that saturation is reached when the surface pressure of the adsorbed gas reaches some definite value : the temperature coefficient of the adsorption maximum would then be of the same order of magnitude as the coefficient of expansion of a gas. The actual experimental values are said to fit in roughly with this idea : they vary by a factor of about 3, which, however, might be expected, since the proposed criterion of saturation is an indefinite one and can only be very roughly true.

The mobility of adsorbed molecules on the surfaces of solid bodies is a question of some general importance. Experiments [88] on the growth of mercury crystals from the vapour seemed to indicate that there were adsorbed molecules of mercury on the crystal surface, but not part of its structure, and that they possessed mobility. It also appeared that molecules of benzophenone could move over the surface of glass. In the light of these observations, catalytic reactions on a solid surface present a slightly different picture from that of Langmuir's original theory, though the essential kinetic relationships are not profoundly modified. For example, suppose we have small adsorption and proportionality between gas pressure and adsorbed amount for each of two reacting substances A and B. If the molecules of A and B are rigidly held, reaction depends upon their alighting from the gas phase to adjacent positions on the surface: the probability of which is proportional to the product of the two pressures. If A and B are freely mobile they may, on the other hand, seek each other out in the adsorption layer: but, although the mechanism is somewhat different, the probability of an encounter is still proportional to the product of the pressures. In fact, it seems clear that the relation between the probability of reaction and the gaseous concentrations ought to be the same whether the movement of the molecules is realised by translation over the surface or by passage through the gas. Surface mobility is formally equivalent to a shorter time of sojourn on the surface in Langmuir's sense.

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[87] *Z. physikal. Chem.*, 1929, [*A*], **144**, 259; *A.*, 1929, 1376.

[88] M. Volmer and G. Adhikari, *Z. Physik*, 1925, **35**, 170; *Z. physikal. Chem.*, 1926, **119**, 46; *A.*, 1926, 349, 467.

It is by no means certain, however, that the powerful adsorption forces acting between surfaces and reacting gases such as oxygen, hydrogen, or carbon monoxide will allow mobility in any degree comparable with that found in Volmer's experiments. M. Polanyi and K. Welke show that different parts of a charcoal surface are associated with very different adsorption energies, and that the density and mobility of the adsorbed molecules must vary over a correspondingly wide range.[89] Quite probably, the most important cases catalytically are those where very strong binding produces great internal changes in the molecules and also greatly reduces or inhibits mobility. A. A. Balandin [90] has developed an hypothesis originally put forward by R. E. Burk, namely, that in some catalytic reactions the molecules are adsorbed, not at one, but at several points of the surface, and has illustrated the helpfulness of the hypothesis in a number of examples. In reactions where this so-called "multiplet" adsorption is important, mobility must presumably not be great.

This is a convenient place to refer to the work of F. P. Bowden and E. A. O'Connor,[91] who measure the quantity of electricity which must be passed in order to cause a given change in the electrode potential of a cathode immersed in dilute acid. This quantity is assumed to be proportional to the "accessible area" of the cathode. This area is available for the liberation of hydrogen, which can be regarded as a catalytic surface reaction—probably depending on the union of atoms. A fusible alloy and liquid gallium give similar results, indicating that the accessible area of all liquid metals is the same.

A number of novel methods have been used for investigating the nature and structure of surface layers. It is of interest to record some of them, although the results obtained by their application have not yet thrown very much really fresh light on the matter. When electrons are diffracted by a solid they penetrate it to a very small extent only. Thus the diffraction effects yield information about the surface layers. G. P. Thomson and C. G. Fraser[92] have described a suitable apparatus for such investigations, and Thomson[93] gives an account of exploratory experiments with different surfaces. E. Rupp[94] has measured the electron waves diffracted by metal surfaces charged with adsorbed gases, and obtained definite effects due to the gases, while he and E. Schmid,[95] applying the method to passive iron, conclude that passivity is determined entirely by the surface layer of atoms. J. Aharoni and F. Simon[96] have measured the magnetic susceptibilities of adsorbed gases, and, among other effects, find a discontinuity in the curve connecting concentration and susceptibility for oxygen adsorbed on carbon : they suggest a transition from a single to a double layer of adsorbed molecules. J. W. McBain and C. R. Peaker,[97] by studying the conductivity due to films of fatty acids on water, show that stearic acid in a unimolecular layer on water of conductivity $1{\cdot}2 \times 10^{-6}$ reciprocal ohms is dissociated to the extent of about one-ninth. Optical methods have been used by J. Perrin[98] and by H. Zocher and F. Stiebel,[99] and a photoelectric method by R. Suhrmann.[99a] H. Dobretsberger[1] finds an increase in the " skin " conductivity for high-frequency currents in platinum wires, on which nitrogen and carbon dioxide are adsorbed, which does not occur with direct current. Hydrogen alters both kinds of conductivity. L. Strohhäcker[2] confirms the unimolecularity of gas layers adsorbed on gold, using a method depending on direct weighing.

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[89] *Z. physikal. Chem.*, 1928, **132**, 371; *A.*, 1928, 580.

[90] For references to this work and a summary, see J. C. W. Frazer, 8th Report of the Committee on Contact Catalysis, *J. Physical Chem.*, 1930, **34**, 2129.

[91] *Proc. Roy. Soc.*, 1930, [*A*], **128**, 317; *A.*, 1131.

Some discussion continues about the appropriate form of the adsorption isotherm, and about the nature of the saturation process. H. W. Foote and J. K. Dixon,[3] working with the systems water or benzene vapour-manganese dioxide, and J. N. Pearce and H. F. Johnstone[4] with methane or its chlorine derivatives-charcoal, find results in agreement with Polanyi's theory. J. W. McBain and G. T. Britton[5] conclude that adsorption by charcoal occurs according to the Langmuir formula and is not adequately represented by any other. On the other hand, M. Crespi and E. Moles[6] conclude that the adsorption of ethylene by glass is in accordance with Freundlich's equation but not with Langmuir's. R. Strömberg[7] finds that the adsorption of water by various surfaces increases to very many molecular layers as the saturation vapour pressure is approached, and J. W. McBain and R. Du Bois[8] find that the amounts of substances carried by bubbles from solutions are several times greater than would correspond to a unimolecular layer of molecules oriented in the surface.

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[92] *Proc. Roy. Soc.*, 1930, [*A*], **128**, 641; *A.*, 1082.

[93] *Ibid.*, p. 649; *A.*, 1082.

[94] *Z. Elektrochem.*, 1929, **35**, 586; *A.*, 1929, 1357; *Ann. Physik*, 1930, [v], **5**, 453.

[95] *Naturwiss.*, 1930, **18**, 459; *A.*, 1230.

[96] *Z. physikal. Chem.*, 1929, [*B*], **4**, 175; *A.*, 1930, 278.

[97] *Proc. Roy. Soc.*, 1929, [*A*], **125**, 394; *A.*, 1929, 1378.

[98] *Kolloid-Z.*, 1930, **51**, 1; *A.*, 687.

[99] *Z. physikal. Chem.*, 1930, **147**, 401; *A.*, 852.

[99a] *Z. Elektrochem.*, 1929, **35**, 681; *A.*, 1929, 1359.

[1] *Z. Physik*, 1930, **65**, 334; *A.*, 1505.

[2] *Ibid.*, 1930, **64**, 248; *A.*, 1364.

[3] *J. Amer. Chem. Soc.*, 1930, **52**, 2170; *A.*, 990.

The conclusion to be drawn from all these observations is probably that, while the Langmuir theory represents the ideal to which many actual examples approximate, the complexity of structure of many surfaces, the existence of capillary condensation, and multiple layer formation in the neighbourhood of the condensation point of vapours introduce complications making it necessary almost always to determine by *ad hoc* experiments the adsorption isotherms and saturation limits for a particular system, the behaviour of which is required for practical purposes to be known.

Many papers have been published dealing with the specific relations of particular adsorption systems. However valuable these may be as contributions to the inorganic chemistry of surfaces, it is impossible to summarise them under a single heading. Certain general tendencies have, however, been evident. One interesting point is the influence of adsorbed "permanent" gases on the adsorption capacity of charcoal for vapours and substances in solution. A. J. Allmand and R. Chaplin,[9] in the course of a detailed study of adsorption by various charcoals, found that traces of foreign gases on the surface of the charcoal have a very great influence on the isotherms of carbon tetrachloride vapour at relatively low pressure. Gradual elimination of gases causes a drift in the adsorption, no final steady value being attained until the displacement is complete. A freshly prepared active charcoal is poisoned by oxygen, the poisoning being greatest at the most active

[4] *J. Physical Chem.*, 1930, **34**, 1260; *A.*, 989.

[5] *J. Amer. Chem. Soc.*, 1930, **52**, 2198; *A.*, 990.

[6] *Anal. Fis. Quim.*, 1930, **28**, 448; *A.*, 990.

[7] *Kungl. Svenska Vetenskapsakad. Handl.*, 1928, **6**, [2], 1; *A.*, 151.

[8] *J. Amer. Chem. Soc.*, 1929, **51**, 3534; *A.*, 152.

[9] A. J. Allmand and R. Chaplin, *Proc. Roy. Soc.*, 1930, [*A*], **129**, 235; *A.*, 1513.

points on the surface. The oxygen is gradually replaced, by the action of the carbon tetrachloride, in the form of carbon monoxide or dioxide. The displacing action of a vapour such as carbon tetrachloride appears sometimes to remove oxygen more effectively than evacuation.

The chemical mechanism of adsorption also presents problems of interest. The adsorption of electrolytes by charcoal is supposed by N. Schilov [10] to depend upon oxide films, two " basic oxides " and an " acidic oxide " being assumed to exist on the surface. A. Frumkin [11] takes the view that charcoal adsorbs ions from solution in virtue of behaving like a gas electrode. Charcoal degassed in a vacuum for 48 hours at 1000° would not adsorb hydrogen chloride or sodium hydroxide. On addition of oxygen, the adsorption capacity for the former reappeared, the amount taken up being chemically equivalent to the amount of oxygen supplied. It is supposed that the adsorbed oxygen sends hydroxyl ions into solution, these being replaced at the surface by the acid anions : $C_xO + H_2O \longrightarrow C_x + 2\oplus + 2OH'$. When, on the other hand, the charcoal is heated in hydrogen, all the above effects are reversed. The charcoal is now supposed to be able to send hydrions into solution, remain with a negative charge, and thus to adsorb kations. It does, in fact, now take up alkali but not acid. These effects are all much increased by the presence of a little platinum in the charcoal, which is not surprising—indeed it would be useful to know that the effects all occur quite definitely in the entire absence of any platinum. Other observers have found that alkali can be taken up by charcoal which had been heated in air to 400°. Frumkin says that different forms of oxygen union must exist (compare Schilov, above), one of which can send hydrions into solution in presence of water.

While these phenomena of ionic exchange are very interesting and probably occur by the mechanism which Frumkin suggests, they cannot give the whole picture of charcoal adsorption : indeed, the phenomenon may be a rather specialised one. H. J. Phelps and R. A. Peters[12] showed that pure ash-free charcoal adsorbs weak organic acids and bases predominantly in the form of un-ionised molecules, the adsorption of acids decreasing with increasing p_H

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[10] *Kolloid-Z.*, 1930, **52**, 107; *A.*, 1108; N. Schilov and K. Tschmutov, *Z. physikal. Chem.*, 1930, **148**, 233; *A.*, 991; N. Schilov, H. Schatunovskaja, and K. Tschmutov, *ibid.*, p. 211; **150**, 31; *A.*, 1364.

[11] *Kolloid-Z.*, 1930, **51**, 123; *A.*, 683; B. Bruns and A. Frumkin, *Z. physikal. Chem.*, 1929, **141**, 141; *A.*, 1929, 640; 1930, **147**, 125; *A.*, 684; R. Burstein and A. Frumkin, *ibid.*, 1929, [*A*], **141**, 158; *A.*, 1929, 640; R. Burstein, *ibid.*, p. 219; *A.*, 1929, 640.

[12] *Proc. Roy. Soc.*, 1929, [*A*], **124**, 554; *A.*, 1929, 1000.

and that of bases increasing in approximate accordance with the change in the number of undissociated molecules present. The Frumkin or Schilov mechanisms could be applied to explain the adsorption of the acids, but not that of bases as well. H. J. Phelps [13] has found that two distinct phenomena, kation exchange in the surface, and adsorption of un-ionised molecules, both play a part in the adsorption of weak electrolytes by fullers' earth.

Discussion of J. J. Thomson's principle that "if surface tension increases as the chemical action goes on, the capillarity will tend to stop the reaction" has been revived by H. Freundlich.[14] The reaction $CH_2Br{\cdot}CH_2{\cdot}NH_2 = NH(CH_2)_2 + HBr$ and its reverse reaction, taking place at the surface of charcoal, were studied in various solutions, neutral, acid, or alkaline, and the adsorptions of the various bases and salts concerned were determined. The influence of the charcoal could be correctly predicted, by Thomson's rule, from the surface tension lowerings indicated by the corresponding adsorptions. An interesting example of the displacement of a chemical equilibrium at an interface may here be referred to: D. Deutsch [15] found that solutions of indicators near to the changing point alter in colour when emulsified with an indifferent liquid, and return to their original state when the phases separate again.

Chemical Kinetics : Chain Reactions.

The prominent part played by the chain-reaction mechanism [16] in the processes of chemical change has become very evident during the last few years. The conditions determining the starting and stopping of reaction chains are becoming more clearly understood, and, incidentally, the canonical classification of reactions into definite "orders" is losing much of its significance.

The criteria by which a chain reaction may be recognised are as follows: (1) in photochemical reactions, an abnormally great quantum yield; (2) in thermal reactions, a retardation of the change by a decrease in the dimensions of the vessel, allowing a smaller path for chains to traverse before reaching the wall; (3) acceleration of the reaction, in some circumstances, by the presence of an inert gas—essentially the inverse of (2); (4) an abnormal influence of the concentrations of the reacting substances on the rate, due to the circumstance that the concentrations affect, not only the number of chains starting in unit time, but also the successfulness of their propagation; (5) a rate of reaction considerably greater than might be expected from a knowledge of the heat of activation and the collision number; (6) sensitiveness of the reaction to inhibitors; (7) in certain examples a very remarkable phenomenon makes its appearance, namely, an abrupt transition at a certain concentration from negligibly slow reaction to explosion. It must be emphasised that all these characteristics are not necessarily or even commonly shown by the same reaction, but examples of all are known.

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[13] *Chem. and Ind.*, 1930, **49**, 516 (Proc. of Biochem. Soc.).

[14] H. Freundlich and F. Juliusberger, *Z. physikal. Chem.*, 1930, **146**, 321; *A.*, 552; H. Freundlich, *J.*, 1930, 164; *A.*, 687.

[15] For references, see *idem*, *ibid*.

[16] See *Ann. Reports*, 1927.

Which characteristics appear in a given reaction depends upon the length of the chain, and upon the manner of its starting and stopping. We may tabulate matters as follows: chains may start either (*a*) in the gas phase or (*b*) at the wall of the vessel. They may be stopped either (α) by a collision in the gas phase with chemical destruction of an active molecule or (α') by a collision in the gas phase with "physical" deactivation of an active molecule; (β) by simple collision of an active molecule with the wall of the vessel, or (γ) by a chemical reaction at the wall of the vessel, removing an active molecule.

Furthermore, chains may be classified as "energy" chains or "material" chains. In the former, the entities responsible for propagating the chain are merely excited molecules of a reactant or product, while in the latter some definite new molecular species, active in virtue of its chemical unsaturation, *e.g.*, a chlorine atom or a hydroxyl radical, is the virtual carrier of the energy.

It will be convenient to discuss some of the reactions actually investigated in the light of the above classification.

First may be mentioned the continuation of Lind's work on the comparison between photochemical reactions of high quantum yield and the corresponding reactions induced by α-particles. The synthesis of carbonyl chloride,[17] the chlorination of benzene, and the oxidation of sodium sulphite by oxygen [18] are reactions in which the yield per quantum is nearly equal to the yield per ion-pair over a wide range of experimental conditions. This shows that, after differently initiated primary processes, similar chains, often of great length, are propagated. The temperature coefficients of the synthesis of hydrogen chloride by white light and by α-particles have also been found to be identical.[19] It is further to be noted that in the photochemical reaction of hydrogen and oxygen and of carbon monoxide and oxygen the temperature coefficients increase with temperature,[20] and the reactions deviate markedly from the Arrhenius equation in the region of temperature where the chain length begins to increase by thermal processes following the initial photochemical act.

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[17] H. N. Alyea and S. C. Lind, *J. Amer. Chem. Soc.*, 1930, **52**, 1853; *A.*, 871.

[18] H. N. Alyea, *ibid.*, p. 2743; *A.*, 1136.

[19] S. C. Lind and R. Livingston, *ibid.*, p. 593; *A.*, 434.

[20] G. B. Kistiakowsky, *Proc. Nat. Acad. Sci.*, 1929, **15**, 194; *A.*, 1929, 659.

The thermal decomposition of chlorine dioxide takes place at 40° at a rate approximately proportional to the square root of the dioxide concentration and to the first power of the total pressure. If the velocity exceeds a certain limit, the decomposition becomes explosive: various gases accelerate the reaction by increasing the total pressure. There is a fairly marked wall influence, which H. J. Schumacher and G. Stieger[21] interpret by assuming that reaction chains both start and stop at the wall. They suggest $ClO_2 \longrightarrow ClO + O$ as the primary process, but not on very direct evidence. The thermal reaction between chlorine and ozone[22] appears to involve chains of about 10^4 links under normal conditions of experiment. The net result of the reaction is a catalytic decomposition of the ozone, the rate of which, after an induction period, is proportional to $[Cl_2]^{\frac{1}{2}}[O_3]^{\frac{3}{2}}$. The mechanism proposed is as follows: $Cl_2 + O_3 = ClO + ClO_2$; $ClO_2 + O_3 = ClO_3 + O_2$; $ClO_3 + O_3 = ClO_2 + 2O_2$; $ClO_3 + ClO_3 = Cl_2 + 3O_2$; $ClO + ClO = Cl_2 + O_2$.

In the ideal case of a chain reaction occurring in a long cylindrical tube, all the chains starting in the gas and being broken at the wall, the rate of reaction should be proportional to the square of the radius of the tube. The ideal conditions are not realised in practice, but a rough approximation to this kind of behaviour is found in the oxidation of methyl alcohol vapour.[23] On the other hand, the rate of oxidation of benzene vapour is almost independent of the dimensions of the vessel until these become very small: thus most of the chains appear to be broken in the gas. It is also becoming evident that adsorbed gas layers profoundly modify the capacity of walls to break chains: this suggests (γ), above, as a commoner mechanism than (β).

The discovery by Chapman that the photochemical combination of hydrogen and chlorine takes place more slowly in a capillary tube than in a wide tube shows that the chains end at the vessel wall—Chapman expresses this by saying that the catalyst formed by the light is destroyed at the wall. D. L. Chapman and P. P. Grigg,[24] by a quantitative analysis of the problem, estimate the mean life of the "catalyst" in the electrolytic gas at normal pressure to be of the order 10^{-2} sec. under the conditions of their experiments, but to be proportional to the sensitivity of the mixture over a wide range. They also establish the important fact that the well-known inhibition of the reaction by oxygen becomes relatively less important the smaller the containing tube. Oxygen normally breaks the chains by deactivation in the gas phase : when the radius of the tube is small enough, wall deactivation is so great that inhibition by oxygen is relatively insignificant.

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[21] *Z. physikal. Chem.*, 1930, [*B*], **7**, 363; *A.*, 708.

[22] M. Bodenstein, E. Padelt, and H. J. Schumacher, *ibid.*, 1929, [*B*], **5**, 209; *A.*, 1929, 1394.

[23] R. Fort and C. N. Hinshelwood, *Proc. Roy. Soc.*, 1930, [*A*], **129**, 284; *A.*, 1529.

[24] *J.*, 1928, 3233; 1929, 2426; *A.*, 1929, 154; 1930, 46.

An interesting point in connexion with the action of inhibitors in photochemical reactions arises in the work of E. J. Bowen and E. L. Tietz [25] on the oxidation of liquid acetaldehyde. In the absence of inhibitors the reaction rate is proportional to the square root of the light intensity : in the presence of the inhibitor the reduced rate is proportional to the first power of the light intensity. The explanation is as follows : The chain-producing substance is peracetic acid, AO_2, initially formed from the aldehyde, A, at a rate proportional to $[A][O_2]\{\text{Intensity}\}$, and, in the uninhibited reaction, finally destroyed by a bimolecular process at a rate proportional to $[AO_2]^2$. Since the number of chains started must equal the number broken, these two rates may be equated; whence $[AO_2] \propto \{\text{Intensity}\}^{\frac{1}{2}}$, and the total rate of reaction is proportional to this. When the inhibitor is present, the chain-breaking mechanism acts at a rate proportional to $[AO_2][A]$ instead of $[AO_2]^2$; whence it follows that $[AO_2]$ and the total reaction rate $\propto$ {Intensity}. Under certain conditions, the photochemical decomposition of hydrogen peroxide solutions [26] is proportional to $\{\text{Intensity}\}^{\frac{1}{2}}$. If the chains are initiated by oxygen atoms or hydroxyl radicals, they would appear to be broken rather by the recombination of these atoms or groups than by reaction with a foreign substance.

A number of investigations have been devoted to the oxidation of hydrocarbons and their simple derivatives, including ethylene,[27] benzene,[28] acetylene,[29] methane,[30] methyl alcohol,[30] formaldehyde,[30, 31] benzaldehyde,[31] and ethane.[32] Usually the rate is decreased by diminution in the diameter of the containing vessel, though to varying degrees (see above [23]). There is often a more or less well-defined "induction period" during which peroxides or aldehydic substances are produced. But the most remarkable characteristic is perhaps the influence of the various concentrations on the rate of oxidation. In all cases the influence of oxygen is relatively small, and in certain circumstances oxygen may actually retard the oxidation. On the other hand, the rates increase rapidly with the concentration of the combustible gas, sometimes approximately as the cube of its concentration. This suggests that intermediate oxygenated products (peroxides or aldehydic substances) occur, and that the chains are continued when these collide with fresh molecules of the combustible gas but are broken when they collide with oxygen. Sometimes, *e.g.*, with methyl alcohol, it appears that the deactivating influence of oxygen is exercised principally in the adsorbed layer at the vessel wall. The exact chemical constitution of the substances responsible for setting up the chains is at present an open question. It should be mentioned that the oxidation of ethylene is sensitised by ozone.[33]

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[25] *J.*, 1930, 234; *A.*, 434.

[26] A. J. Allmand and D. W. G. Style, *J.*, 1930, 596; *A.*, 715.

[27] H. W. Thompson and C. N. Hinshelwood, *Proc. Roy. Soc.*, 1929, [*A*], **125**, 277; *A.*, 1929, 1243.

[28] R. Fort and C. N. Hinshelwood, *ibid.*, 1930, [*A*], **127**, 218; *A.*, 709.

[29] G. B. Kistiakowsky and S. Lenher, *J. Amer. Chem. Soc.*, 1930, **52**, 3785; *A.*, 1528.

[30] R. Fort and C. N. Hinshelwood, *Proc. Roy. Soc.*, 1930, [*A*], **129**, 284; *A.*, 1529.

[31] P. J. Askey, *J. Amer. Chem. Soc.*, 1930, **52**, 974; *A.*, 547.

[32] W. A. Bone and S. G. Hill, *Proc. Roy. Soc.*, 1930, [*A*], **129**, 434.

Between 520° and 600°, and above a certain pressure, chains are propagated in mixtures of hydrogen and oxygen, in such a manner as to give a reaction rate very sensitive to the pressure of both gases, but especially that of the hydrogen, and to the diameter of the vessel.[34] They appear to be broken at the wall, and it has been suggested that they are initiated by a termolecular reaction, $2H_2 + O_2$, though this is simply a convenient working hypothesis. At lower pressures the explosion phenomenon referred to under (7) above makes its appearance.[35] Between two well-defined limits of pressure (dependent on the temperature), explosion takes place, while outside these limits there is relatively slow combination. Between the limits, chains, evidently somewhat different in character from those propagated at higher pressures, are set up, and "branch," leading to explosion in the manner described by N. Semenov [36] and exemplified in the explosive oxidation of phosphorus and sulphur vapours. The lower pressure limit is probably that where chains are broken at the wall rapidly enough to prevent their effective multiplication by branching, and the upper limit occurs where they are broken by deactivation in the gas phase. H. N. Alyea and

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[33] R. Spence and H. S. Taylor, *J. Amer. Chem. Soc.*, 1930, **52**, 2399; *A.*, 1000.

[34] C. N. Hinshelwood and H. W. Thompson, *Proc. Roy. Soc.*, 1928, [*A*], **118**, 170; *A.*, 1928, 483; C. H. Gibson and C. N. Hinshelwood, *ibid.*, **119**, 591; *A.*, 1928, 960.

[35] H. W. Thompson and C. N. Hinshelwood, *ibid.*, 1929, [*A*], **122**, 610; *A.*, 1929, 403; D. Kopp, A. Kovalsky, A. Sagulin, and N. Semenov, *Z. physikal. Chem.*, 1930, [*B*], **6**, 307; *A.*, 299.

[36] *Ibid.*, 1929, [*B*], **2**, 169; *A.*, 1929, 514.

F. Haber [37] have found that streams of hydrogen and oxygen, meeting at right angles and mixing in an atmosphere of nitrogen, fail to ignite, under conditions of temperature and partial pressure apparently suitable for the purpose, unless a solid surface is interposed in their path. It seems, therefore, that the first centres from which the chains are propagated are formed in a surface reaction. With regard to the nature of the process initiating the chains, two views have been expressed. According to one, hydrogen peroxide molecules are first formed, whereas according to K. F. Bonhoeffer and F. Haber,[38] the primary reaction is $H_2 + O_2 = 2OH$. This is followed by $OH + H_2 = H_2O + H$, and $H + O_2 + H_2 = OH + H_2O$. This scheme is based upon the appearance of the OH bands in the spectrum of hydrogen–oxygen flames and in the absorption spectrum of steam at 1250°, upon an analysis of the various reactions thermochemically possible,[38a] and upon the fact that hydrogen atoms produced in an electric discharge can cause hydrogen–oxygen mixtures to explode. It must be remarked, however, that 1250° is as much above the temperature where experiments on the rate of combination are made as 0°, where hydrogen peroxide can be condensed out of the flame, is below it. Thus the matter must be regarded as not entirely settled.

Analogous results have been found by H. W. Thompson [39] for the combustion of carbon disulphide in oxygen, namely, an upper and a lower pressure limit, between which explosion occurs, and a dependence of the explosions on the presence of a solid surface. Thompson also records a number of observations on an induction period, and on the variation of the explosion pressure with surface conditions.

Similar " limit " phenomena occur in the oxidation of phosphine : the upper limit depends on gas deactivation, and is independent of the diameter of the vessel ; while the lower depends on the diameter in the way predicted by theory, assuming wall deactivation. The lower limit is displaced by ultra-violet light, owing to the production of minute traces of a substance which exerts an effect analogous to that of nitrogen peroxide on mixtures of hydrogen and oxygen.[40] L. Farkas, F. Haber, and P. Harteck [41] find that small amounts of ammonia sensitise the combustion of hydrogen and of carbon monoxide when illuminated by ultra-violet light; further observations of an analogous kind are recorded by L. Farkas and P. Harteck.[42]

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[37] D. Kopp, A. Kovalsky, A. Sagulin, and N. Semenov, *Z. physikal. Chem.*, 1930, [*B*], **10**, 193 ; *A.*, 1528.

[38] *Ibid.*, 1928, [*A*], **137**, 263 ; *A.*, 1929, 11.

[38a] Compare also E. H. Riesenfeld and E. Wassmuth, *ibid.*, 1930, [*A*], **149**, 140 ; *A.*, 1126.

[39] *Ibid.*, 1930, [*B*], **10**, 273.

[40] R. H. Dalton and C. N. Hinshelwood, *Proc. Roy. Soc.*, 1929, [*A*], **125**, 294 ; *A.*, 1929, 1243 ; R. H. Dalton, *ibid.*, 1930, [*A*], **128**, 263 ; A., 1127 ; K. Clusius and C. N. Hinshelwood, *ibid.*, 1930, [*A*], **129**, 589.

[41] *Z. Elektrochem.*, 1930, **36**, 711 ; *Naturwiss.*, 1930, **18**, 266 ; *A.*, 554.

B. Topley [43] and also Semenov [44] report the existence of limits in the oxidation of carbon monoxide in the presence of water vapour. The influence of hydrogen and of water vapour on the ignition of carbon monoxide has been studied by V. E. Cosslett and W. E. Garner,[45] and by A. Smithells, H. Whitaker, and T. Holmes.[46]

The Occurrence of Free Atoms.

As pointed out in an earlier section, activation of molecules for chemical change involves the excitation of the vibrational degrees of freedom, the limiting stage of this process being the resolution of the molecule into atoms. Activation does not always go to this extreme limit. For example, the heat of dissociation, thermally measured, of hydrogen iodide is 69,000 calories, but the heat of activation of the process $2HI = H_2 + I_2$ is only 44,000 calories. In a number of reactions, however, the activation goes to the limit and free atoms play a part. This occurs especially in photochemical reactions; but it is not justifiable, without direct evidence, to transfer conclusions drawn from observations of photochemical behaviour to thermal reactions. In recent years many specific mechanisms for chemical reactions have been suggested, involving the participation of free atoms and radicals, the latter sometimes of hitherto unknown structures. While these suggestions are all of interest, and often valuable as working hypotheses, it is usually desirable to scrutinise them closely. It would, indeed, be an advantage if specific evidence were occasionally more clearly stated.

Among the reactions where free atoms have been definitely shown to intervene, those involving halogens are especially important. Further interesting work by A. Berthoud [47] and others on the photochemical isomerisation of *allo*cinnamic acid in the presence of iodine and on the photobromination of unsaturated compounds yields evidence (*e.g.*, proportionality of rate to square root of light intensity) that free halogen atoms are formed in these reactions. R. M. Purkayastha and J. C. Ghosh, [48] comparing the thermal and the photochemical bromination of organic hydroxy-acids, conclude that in the former active bromine molecules, whilst in the latter bromine atoms, are concerned.

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[42] *Naturwiss.*, 1930, **18**, 443; *A.*, 1260. [43] *Nature*, 1930, **125**, 560; *A.*, 547.

[44] See ref. 35 (p. 45), second part.

[45] *Trans. Faraday Soc.*, 1930, **26**, 190; *A.*, 708.

[46] *J.*, 1930, 185; *A.*, 428.

[47] *Helv. Chim. Acta*, 1930, **13**, 385; *A.*, 718; A. Berthoud and C. Urech, *J. Chim. physique*, 1930, **27**, 291; *A.*, 1260; *Helv. Chim. Acta*, 1930, **13**, 437; *A.*, 1136.

[48] *Z. physikal. Chem.*, 1930, [*B*], **7**, 276, 285; *A.*, 718.

It is interesting to note that the chlorine atoms formed by the dissociation of iodine chloride will not, apparently, cause combination between chlorine and hydrogen, a normal atom being supposed to result from this dissociation, while atoms in the $^2P_1$ state are required for the formation of hydrogen chloride.[49]

The theory of Bonhoeffer and Haber that hydrogen atoms and hydroxyl radicals play a part in the combustion of hydrogen has already been mentioned. G. B. Kistiakowsky [50] has studied the formation of hydrogen peroxide and ozone by the action of the oxygen atoms which he supposes to be formed when hydrogen–oxygen mixtures are illuminated by light of short wave-length. H. Klinkhardt and W. Frankenburger,[51] studying the production of hydrogen peroxide by the atomic hydrogen formed under the influence of the mercury resonance line, assume the processes $H + O_2 + H_2O = H_2O_2 + OH$ and $2OH + M = H_2O_2 + M$, M being a third molecule.

The Stern–Gerlach experiment, carried out with active nitrogen,[52] gives evidence of a constituent with a magnetic moment corresponding to a nitrogen atom in the metastable $^2P_{\frac{1}{2}}$ state (3·5 volts). The active nitrogen problem now stands approximately as follows. Kinetic measurements on the whole indicate that the glow-producing decay depends upon a three-body collision between two atoms and a molecule. Decay can, however, also take place in a non-luminous manner on the walls of the vessel; and the "poisoning" of the walls by a foreign substance is necessary for the production of the glow. E. J. B. Willey [53] finds the "order" of the decay process to vary with the state of the walls, and gives other evidence in favour of regarding as wall poisons those substances which favour the persistence of the luminescence. The actual carrier of the glow is a nitrogen molecule excited to an energy of about 11·5 volts. H. Sponer [54] had supposed this energy to be given to an N_2 molecule in the process $N + N + N_2 = N_2' + N_2$. But 11·5 volts is greater than the dissociation energy of nitrogen (9·1 volts) and thus the molecules cannot be excited in a single act of recombination. G. Cario and J. Kaplan [55] suggest that the 11·5-volt molecules are formed by collisions between a first-formed metastable molecule of 8 volts energy ($^3\Sigma$ state) and a metastable atom in the ^2P state. This view is supported by the results of Jackson and Broadway. To explain the abnormal distribution of intensity among the bands of the glow, Cario and Kaplan also assume that interaction between metastable molecules and metastable atoms of 2·4 volts (^2D state) gives rise to excited molecules which contribute to the luminescence.

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[49] G. K. Rollefson and F. E. Lindquist, *J. Amer. Chem. Soc.*, 1930, **52**, 2793; *A.*, 1135.

[50] *Ibid.*, p. 1868; *A.*, 871.

[51] *Z. physikal. Chem.*, 1930, [*B*], **8**, 138; *A.*, 1004.

[52] L. C. Jackson and L. F. Broadway, *Proc. Roy. Soc.*, 1930, [*A*], **127**, 678; *A.*, 969.

[53] *J.*, 1930, 336, 1146; *A.*, 524, 838.

[54] *Z. Physik*, 1925, **34**, 622; *A.*, 1926, 8.

[55] *Ibid.*, 1929, **58**, 769; *A.*, 1930, 124.

The combination of hydrogen atoms should take place in the gas phase in triple collisions $2H + M = H_2 + M$. The process is much complicated by wall influences, as with active nitrogen, but observations appear to confirm the triple-collision hypothesis in a general way, though without anything approaching quantitative completeness.[56] In addition to examples mentioned elsewhere in this Report, a good deal of work has been carried out on the actual chemical reactions of atomic oxygen, nitrogen, and hydrogen produced either photochemically or by Wood's method.[57]

A. Farkas [58] finds that the thermal transformation of parahydrogen into the equilibrium mixture of ortho- and para- can take place at high temperatures as a homogeneous gas reaction. The order of the reaction is 1·5. This suggests the mechanism $H_2^{para} + H \rightleftharpoons H + H_2^{ortho}$, the hydrogen atoms which provoke the change being those produced by the normal thermal dissociation of hydrogen molecules.

A good deal of work has been carried out on chemical actions in electric discharges. Free atoms sometimes, but not always, play an important part. In interpreting their experiments on the "cathodic" combustion of carbon monoxide, Finch and others [59] make use of the hypotheses that carbon monoxide molecules are excited in the discharge, but not actually ionised, and that the principal process occurring in the direct oxidation is a triple collision between a carbon monoxide molecule, an oxygen atom, and a third molecule or an electron. When the electrode "sputters," it is supposed that metal atoms are produced and that these combine with oxygen to form "complexes" which readily oxidise the combustible gas. A. K. Brewer and J. W. Westhaver,[60] investigating the relative amounts of chemical reaction produced in different parts of a discharge, and the influence of foreign gases, conclude that the ion N_2^+ is the principal agent in the formation of ammonia or of nitrogen peroxide from their respective elements, atoms being ineffective : the O_2^+ ion is the chief agent in ozone formation. A great variety of entities are formed in an electric discharge,[61] the gases mentioned yielding according to circumstances, O_2^+, O^+, CO^+, C^+, CO_2^+, N_2^+, N^+, H_2^+, H^+, neutral atoms, NH, or NH_2. Thus it is not to be wondered at that the interpretation of experimental evidence is a complicated matter. O. H. Wansbrough Jones,[62] studying the formation of oxides of nitrogen and of ozone under the influence of electrons accelerated by known voltages, concludes, in general agreement with Brewer, that in the former reaction the excitation of the nitrogen is alone important, the principal processes being $N_2^+ + O_2 = 2NO$ and $N^+ + O_2 = NO_2$.

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[56] H. Senftleben and O. Riechemeier, *Physikal. Z.*, 1929, **30**, 745; *A.*, 1930, 166; *Naturwiss.*, 1930, **18**, 645; *A.*, 1126.

[57] *E.g.*, H. C. Urey and G. I. Lavin, *J. Amer. Chem. Soc.*, 1929, **51**, 3286; *A.*, 1930, 46; A. Klemenc and F. Patat, *Naturwiss.*, 1930, **18**, 281; *A.*, 554; P. Harteck and U. Kopsch, *Z. Elektrochem.*, 1930, **36**, 714; *A.*, 1388; W. Frankenburger *et al.*, *ibid.*, p. 757; *A.*, 1383.

[58] *Z. physikal. Chem.*, 1930, [*B*], **10**, 419.

[59] G. I. Finch and H. H. Thompson, *Proc. Roy. Soc.*, 1930, [*A*], **129**, 314; G. I. Finch and W. L. Patrick, *ibid.*, p. 656.

[60] *J. Physical Chem.*, 1930, **34**, 153, 554, 1280; *A.*, 304, 553, 1003.

The Chemistry of Hydrogen and Hydroxyl Ions.

The following new method has been proposed for determining the ionic product of water.[63] The constant, K, of the equilibrium set up when mercuric oxide, mercury, mercurous bromide, and potassium bromide are shaken together is measured by analysis of the hydroxyl- and bromine-ion concentrations of the resulting solution.

(1) $\frac{1}{2}HgO(\text{solid}) + \frac{1}{2}Hg(\text{liquid}) + \frac{1}{2}H_2O(\text{liquid}) + Br' = \frac{1}{2}Hg_2Br_2(\text{solid}) + OH'$.

The *E.M.F.* of the cell Hg,HgO(solid),OH′,H_2,Pt, corresponding to the process

(2) $\frac{1}{2}Hg(\text{liquid}) + \frac{1}{2}H_2O(\text{liquid}) = \frac{1}{2}HgO(\text{solid}) + \frac{1}{2}H_2$,

and that of the cell Pt,H_2,H^+,Br′,Hg_2Br_2(solid),Hg(liquid), corresponding to the process

(3) $\frac{1}{2}H_2 + \frac{1}{2}Hg_2Br_2(\text{solid}) = H^+ + Br' + Hg(\text{liquid})$,

are measured. The values E_2 and E_3 of the free energies of processes (2) and (3) for unit activity of H^+ or OH′ or Br′ are calculated. The sum of processes (1), (2), and (3) gives

(4) $H_2O(\text{liquid}) = H^+ + OH'$.

Since the free energy of process (1) is $RT \log a_{OH}/a_{Br} - RT \log K$, *i.e.*, $-RT \log K$ for unit OH′ and Br′ activities, the free energy of (4) is known. This quantity is also equal to $RT \log a_{\mathrm{H}} \cdot a_{\mathrm{OH}} - RT \log K_w$, *i.e.*, to $-RT \log K_w$ for the unit activities to which the other terms in the sum refer. Thus K_w is found. The value obtained experimentally was $1{\cdot}02 \times 10^{-14}$ at 25°.

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[61] H. Kallmann and B. Rosen, *Z. Physik*, 1929, **58**, 52; 1930, **61**, 61; *A.*, 1930, 16, 514; H. D. Smyth and E. C. G. Stueckelberg, *Helv. Phys. Acta*, 1929, **2**, 303; *A.*, 1930, 975; G. I. Lavin and J. R. Bates, *Nature*, 1930, **125**, 709.

[62] *Proc. Roy. Soc.*, 1930, [*A*], **127**, 511, 530; *A.*, 1000.

[63] R. F. Newton and M. G. Bolinger, *J. Amer. Chem. Soc.*, 1930, **52**, 921; *A.*, 542.

As Brönsted has shown, "acid catalysis" is not exclusively a function of the hydrion, *i.e.*, in aqueous solution of the ion H_3O^+; and, indeed, Brönsted was led by his experimental studies, as well as by general theoretical considerations, to propose a new definition of an acid, namely, any substance which may lose a proton. This means that the method for the determination of hydrion concentration by observation of the catalytic effect on a reaction velocity must be used with circumspection. It is interesting, however, that J. N. Brönsted and C. Grove [64] have now found the hydrolysis of dimethylacetal to proceed at a rate directly proportional to the concentration of the ion H_3O^+, and not to be catalysed appreciably by other "acids." This reaction is therefore useful for the determination of hydrion concentration.

In connexion with acid and basic catalysis, an interesting point emerges from considerations put forward by C. K. Ingold,[65] who distinguishes two factors determining the case of hydrolysis of esters, namely a "polar" effect and a "steric" effect. No relation can be traced between the rate of hydrolysis of different esters and the "polar" properties of substituent groups contained in them: this he attributes to the fact that the different shapes of the molecules ("steric factor") mask any regularity. The *relative* influence of a negatively charged hydroxyl and a positively charged hydrion in catalysing the hydrolysis of the same ester should be independent of the shape of the molecule, but not of the "polarity." And, in fact, Ingold finds that the ratio of the velocity coefficients for catalysis by hydrion and hydroxyl ion respectively for a series of esters shows a regular trend with changing polarity of substituent groups.

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[64] *J. Amer. Chem. Soc.*, 1930, **52**, 1394; *A.*, 711.

[65] *J.*, 1930, 1032; *A.*, 868.

INORGANIC CHEMISTRY

Although no work of outstanding importance has appeared, there is a distinct improvement in the papers on Inorganic Chemistry which have been published during the past year, both as regards the quality of the work and the conciseness of its presentation.

A tendency is apparent in some quarters towards duplication or even triplication of publication—in journals of different types. This has several undesirable consequences: it swells the bulk of journal literature unnecessarily, and it results either in several abstracts of what is really the same work or in an abstract of the first paper only, which is itself usually more or less in the nature of an abstract.

Atomic Weights and Separation of Isotopes.

It begins to look as though hydrogen may be the only simple element. Carbon,[1] nitrogen,[2] and oxygen [3] all appear to be complex, containing very small proportions of the isotopes C^{13}, N^{15}, and O^{17} and O^{18}. The oxygen isotopes are only present to the extent of about 1 in 10^4 and 1 in 1250 respectively, which is too small to introduce appreciable error when oxygen is taken as the basis of the atomic-weight system.[4] The divergence of the atomic weight of oxygen from 16 is about 1·25 parts in ten thousand.[5] K. P. Jakovlev [6] has reviewed the methods which have been used for the separation of isotopes and has himself designed an apparatus by which it is possible, by using a bundle of positive rays, to separate small quantities of isotopes in a pure condition.

Potassium.—According to H. H. Lowry,[7] the atomic weight of potassium from plant ash is normal, and this lends no support to a remarkable result recorded by F. H. Loring and J. G. F. Druce.[8]

Nitrogen; *Phosphorus.*—The method of limiting densities applied to ammonia[9] and to phosphine[10] has given values of 14·009 and 30·977 for the atomic weights of nitrogen and phosphorus respectively.

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[1] A. S. King and R. T. Birge, *Astrophys. J.*, 1930, **72**, 19; *A.*, 1931, 15.

[2] S. M. Naudé, *Physical Rev.*, 1930, (ii), **36**, 333; *A.*, 1232; G. Herzberg, *Z. physikal. Chem.*, 1930, [*B*], **9**, 43; *A.*, 1084.

[3] R. Mecke and K. Wurm, *Z. Physik*, 1930, **61**, 37; *A.*, 515; E. Rüchardt, *Naturwiss.*, 1930, **18**, 534; *A.*, 975.

[4] E. Moles, *Anal. Fis. Quim.*, 1930, **28**, 127; *A.*, 515.

[5] F. W. Aston, *Nature*, 1930, **126**, 953.

[6] *Z. Physik*, 1930, **64**, 378; *A.*, 1337.

[7] *J. Amer. Chem. Soc.*, 1930, **52**, 4322.

[8] *Chem. News*, 1930, **140**, 34.

Arsenic.—Analysis of arsenic trichloride gave the value 74·936 ± 0·001 for the atomic weight of arsenic.[11]

Vanadium.—The atomic weight of vanadium was found to be 50·947 from a determination of the ratio $VOCl_3 : 3Ag$.[12]

Tantalum.—K. R. Krishnaswami,[13] from a careful determination of the ratios $TaBr_5 : 5Ag : 5AgBr$ and $TaCl_5 : 5Ag : 5AgCl$, finds the atomic weight of this element to be 181·36.

Sulphur.—By synthesising silver sulphide from its elements, O. Hönigschmid[14] finds the atomic weight of sulphur to be 32·0685 ± 0·0006.

Molybdenum.—The mass spectrum of the carbonyl shows that molybdenum has 7 isotopes. From the mass numbers, the approximate abundances, and the packing fractions, the value 95·97 ± 0·05 is calculated for the atomic weight of molybdenum.[15]

Chlorine.—According to A. F. Scott and C. R. Johnson,[16] a direct determination of the solubility of silver chloride in 0—1*M*-nitric acid at 0·5° shows that the value accepted by Hönigschmid and Chan[17] is too low, so that their determination of the atomic weight of chlorine is about 0·001 unit too high.

Rhenium.—The atomic weight of rhenium (188·7) appears for the first time in the Report of the German Commission on atomic weights.[18] Methods available for determining this value have been critically examined by O. Hönigschmid and R. Sachtleben,[19] who obtain the value 186·31 ± 0·02 from the ratio $AgReO_4 : AgBr$.

Intensive Drying.

A paper of considerable importance in connexion with the problem of intensive drying has appeared,[20] in which it is shown that water has an abnormally high activity when present in traces in such liquids as benzene, in which its solubility is very low. Decrease in the vapour pressure of such liquids by intensive drying can be explained by the removal of the abnormally high partial pressure of the water, and there is no need to assume any catalytic effect of the latter on an inner equilibrium.

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[9] E. Moles and T. Batuecas, *Anal. Fis. Quim.*, 1930, **28**, 871; *A.*, 1357.

[10] M. Ritchie, *Proc. Roy. Soc.*, 1930, [*A*], **128**, 551; *A.*, 1104.

[11] J. H. Křepelka, *J. Czech. Chem. Comm.*, 1930, **2**, 255; *A.*, 975.

[12] A. F. Scott and C. R. Johnson, *J. Amer. Chem. Soc.*, 1930, **52**, 2638; *A.*, 1084.

[13] *J.*, 1930, 1277; *A.*, 975.

[14] *Z. Elektrochem.*, 1930, **36**, 689; *A.*, 1337.

[15] F. W. Aston, *Nature*, 1930, **126**, 348; *A.*, 1338.

[16] *J. Amer. Chem. Soc.*, 1930, **52**, 3586; *A.*, 1337.

[17] *Z. anorg. Chem.*, 1927, **163**, 315; *A.*, 1927, 806.

[18] M. Bodenstein, A. Hahn, O. Hönigschmid, and R. J. Meyer, *Ber.*, 1930, **63**, [*B*], 1; *A.*, 269.

[19] *Z. anorg. Chem.*, 1930, **191**, 309; *A.*, 1338.

[20] (Miss) E. J. Greer, *J. Amer. Chem. Soc.*, 1930, **52**, 4191; *A.*, 1931, 34.

Superconductors.

Niobium [21] and ruthenium [22] have been shown to become superconducting between 8·74° and 8·18° Abs. and at 2·04° Abs., respectively. Titanium has almost become a superconductor at 1·16° Abs., and it is considered that many if not all metals are likely to show superconductivity if the temperature is low enough.[23] The conductivities of many metals and alloys have been examined down to temperatures as low as 1·43° Abs., and several superconducting alloys were found,[24] of which Rose's alloy showed a resistance–temperature hysteresis.[25] Titanium nitride (1·2° Abs.), vanadium nitride (1·2°), and the carbides of molybdenum (7°), niobium (10°), and tantalum (9°) become superconducting at the temperatures shown.[26] Niobium carbide shows this phenomenon at a higher temperature than is known for any other substance.

X-*Rays and Chemical Problems.*

It is more and more becoming standard practice to supplement metallographical and other investigations of a chemical nature by an X-ray examination of the substances which are being studied. Zirconium dioxide [27] has been shown in this way to occur in three different varieties. According to W. Morris-Jones and E. G. Bowen,[28] the compound SnSb, which forms good cubic crystals, has a sodium chloride lattice, and so is ionic in structure and probably contains tervalent tin.

Co-ordination.

Equations have been developed by F. J. Garrick [29] which enable him to calculate the maximum co-ordination numbers of uni- and

[21] W. Meissner and H. Franz, *Z. Physik*, 1930, **63**, 558; *A.*, 1102.

[22] J. C. McLennan, *Nature*, 1930, **125**, 168; *A.*, 281; J. C. McLennan, J. F. Allen, and J. O. Wilhelm, *Trans. Roy. Soc. Canada*, 1929, (iii), **23**, III, 283; *A.*, 532.

[23] W. Meissner, *Z. Physik*, 1930, **60**, 181; *A.*, 531.

[24] J. C. McLennan, L. E. Howlett, and J. O. Wilhelm, *Trans. Roy. Soc. Canada*, 1929, (iii), **23**, III, 287; *A.*, 531; W. J. de Haas, E. van Aubel, and J. Voogd, *Proc. K. Akad. Wetensch. Amsterdam*, 1930, **33**, 258; *A.*, 676.

[25] J. C. McLennan, *Nature*, 1930, **125**, 447; *B.*, 616.

[26] W. Meissner and H. Franz, *Naturwiss.*, 1930, **18**, 418; *A.*, 846; *Z. Physik*, 1930, **65**, 30; *A.*, 1507.

[27] W. M. Cohn and S. Tolksdorf, *Z. physikal. Chem.*, 1930, [*B*], **8**, 331; *A.*, 1099.

[28] *Nature*, 1930, **126**, 846; *A.*, 1931, 33.

[29] *Phil. Mag.*, 1930, [vii], **9**, 131; **10**, 76, 77; *A.*, 276, 1096.

bi-valent kations. The assumption is made that the most stable complexes are those in which the electrostatic energy is a maximum and the values so calculated are on the whole in good agreement with Sidgwick's rule.

Corrosion and Passivity of Metals.

Much work on the anodic passification of metals has been published during the past year.[30] The transparent film responsible for the passivity of iron made anodic in dilute sulphuric acid has been isolated.[31] Potential–time curves have been constructed for a number of iron alloys, as well as for iron and aluminium, in order to study the effect of various treatments of the metal on its passivity.[32] The capacity for different anions to penetrate the protective film has been examined,[33] whilst the influence of acids in passivity and corrosion and the reproducibility of results in corrosion work have been considered.[34] The theoretical aspect of corrosion has also been dealt with by F. Tödt.[35] A new explanation of the passivity of iron based on its behaviour as a higher oxide electrode has been put forward.[35a]

Group O.

The m. p.'s of krypton and xenon are −157·0° ± 0·5° and − 112·0° ±0·5° respectively. Solid krypton appears to have a transition point at about −185°.[36] The m. p.'s of hydrogen, neon, and nitrogen have been determined for pressures up to 5000 kg. per sq. cm., and those of argon up to 3400 kg. per sq. cm.[37] The solubilities of helium, neon, and argon for the range 15—37° have been determined in water and several organic solvents.[38]

Group I.

The inner equilibrium of the α- and the β-form of hydrogen has been considered by A. Smits.[39] The conversion of active hydrogen into molecular hydrogen is greatly delayed if the walls of the discharge tube are washed with phosphoric acid. Metallic lead yields a volatile hydride by the action of active hydrogen.[40] Ipatiev has continued his investigations of the displacement of metals from solutions by hydrogen under high pressure, by investigating the case of arsenic.[41] The behaviour of aqueous solutions of a number of nitrates towards hydrogen under pressure has also been examined,[42] as well as the displacement of lead from its organo-metallic compounds.[43]

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[30] W. J. Müller, L. Holleck, K. Konopicky, and W. Machu, *Monatsh.*, 1929, **52**, 409, 425, 442, 463, 474; *A.*, 298.

[31] U. R. Evans, *Nature*, 1930, **126**, 130; *A.*, 1126.

[32] L. C. Bannister and U. R. Evans, *J.*, 1930, 1361; *A.*, 999.

[33] S. C. Britton and U. R. Evans, *ibid.*, p. 1773; *A.*, 1258.

[34] U. R. Evans, *ibid.*, p. 478; *B.*, 462; *Amer. Electrochem. Soc.*, May, 1930, Advance Copy; *B.*, 463.

[35] *Z. physikal. Chem.*, 1930, **148**, 434; *A.*, 1125.

[35a] J. F. Chittum, *J. Physical Chem.*, 1930, **34**, 2267; *A.*, 1527.

[36] K. Peters and K. Weil, *Z. physikal. Chem.*, 1930, **148**, 27; *A.*, 986; F. J. Allen and R. B. Moore, *J. Amer. Chem. Soc.*, 1930, **52**, 4173; *A.*, 1508.

[37] F. Simon, M. Ruhemann, and W. A. M. Edwards, *Z. physikal. Chem.*, 1930, [*B*], **6**, 331; **7**, 80; *A.*, 403, 533.

[38] A. Lannung, *J. Amer. Chem. Soc.*, 1930, **52**, 68; *A.*, 406.

[39] *Proc. K. Akad. Wetensch. Amsterdam*, 1929, **32**, 1118; *A.*, 293; *Physikal. Z.*, 1930, **31**, 172, 178; *A.*, 393.

Small quantities of any of the alkali metals can be obtained by heating such salts as the chromate or dichromate with excess of zirconium in a vacuum.[44]

The vapour density of sodium shows that some Na_2 molecules are present.[45] Metallic sodium and silver iodide or chloride in liquid ammonia solution react sharply in accordance with the equation $Na + AgX = NaX + Ag$.[46] Pure sodium hydride has been prepared [47] as fine white needles by the interaction of hydrogen and sodium vapour at 400—450°. Its heat of formation has been determined.

The melting-point curve of $NaCl,2H_2O$ has been followed up to pressures of 12,000 bars (c. g. s. atmospheres). It passes through a maximum at 25·8° and 9500 bars. The melting point is $+ 0{\cdot}1°$ at 1 bar pressure.[48]

Anhydrous sodium sulphate appears to exist in five different forms,[49] and the existence of three forms of potassium nitrate has been established.[50]

The reaction between sodium hydroxide and metallic oxides $xRO_y + 2NaOH \longrightarrow Na_2R_xO_{(xy+1)} + H_2O$ has been followed by determining the water formed and also, by means of suitable dissolution, the quantity of metallic oxide which has entered into the change. By using excess of alkali hydroxide and of metallic oxide in different experiments, the compounds richest and poorest in alkali can be established with a large measure of certainty. A number of compounds derived from the oxides of Si, Ti, Zr, Ce, Al, Fe, and Cr have been characterised in this way.[51]

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[40] H. von Wartenberg, G. Schultze, and E. Müller, *Z. physikal. Chem.*, 1930, [*B*], **6**, 261; *A.*, 302.

[41] V. Ipatiev, G. Razubaiev, and V. Malinovski, *Ber.*, 1930, **63**, [*B*], 166, 2812; *A.*, 1930, 306; 1931, 52.

[42] V. Ipatiev and B. Muromtzev, *ibid.*, p. 160; *A.*, 306.

[43] V. N. Ipatiev, G. A. Razubaiev, and I. F. Bogdanov, *J. Russ. Phys. Chem. Soc.*, 1929, **61**, 1791; *A.*, 428; *Ber.*, 1930, **63**, [*B*], 335; *A.*, 463.

[44] J. H. de Boer, J. Broos, and H. Emmens, *Z. anorg. Chem.*, 1930, **191**, 113; *A.*, 1136.

[45] W. H. Rodebush and E. G. Walters, *J. Amer. Chem. Soc.*, 1930, **52**, 2654; *A.*, 1104.

[46] W. M. Burgess and E. H. Smoker, *ibid.*, p. 3573; *A.*, 1386.

[47] H. Hagen and A. Sieverts, *Z. anorg. Chem.*, 1930, **185**, 239; *A.*, 307.

[48] L. H. Adams and R. E. Gibson, *J. Amer. Chem. Soc.*, 1930, **52**, 4252; *A.* 1931, 40.

[49] F. C. Kracek and R. E. Gibson, *J. Physical Chem.*, 1930, **34**, 188; *A.*, 281; F. C. Kracek and C. J. Ksanda, *ibid.*, p. 1741; *A.*, 1099.

[50] F. C. Kracek, *ibid.*, p. 225; *A.*, 402.

A careful revision of most of the older work on the polysulphides of sodium has been carried out by T. G. Pearson and P. L. Robinson.[52] The mono-, di-, tri-, tetra-, and penta-sulphides all exist both in the anhydrous condition and hydrated.

The compounds $K_2PbCu(NO_2)_6$, $K_2PbNi(NO_2)_6$, and $K_2PbCo(NO_2)_6$ are obtained by precipitation with potassium nitrite of mixed solutions of lead and copper (or nickel) acetates or of lead and cobalt nitrate.[53] *X*-Ray examination shows that they all have a cubic lattice very similar to that of $K_3Co(NO_2)_6,3H_2O$, from which it is concluded that the 3 molecules of water in the latter compound are zeolitic in character and entangled in the crystal lattice. It is considered that the above lead compounds contain ions of the type $[M(NO_2)_6]''''$, where M is Cu, Co, or Ni. Several complex salts derived from potassium manganese (cobalt or zinc) double oxalates by replacement of C_2O_4 groups by $(NO_2)_2$, $(CNS)_2$, or S_2O_3 have been described.[54]

From an examination of the system iodine–potassium iodide, it is concluded that neither the tri-iodide nor any other polyiodide of potassium can exist as stable solid above 25°.[55] In the case of cæsium, the tetraiodide and the tri-iodide can separate either from melts or from aqueous solutions, but the pentaiodide does not exist.[56]

German carnallite contains, on the average, 0·02% of rubidium chloride and 0·0002% of cæsium chloride, and full details have been published [57] of a comparatively rapid and simple method by which practically the whole of this can be recovered in a high state of purity. The whole of the rubidium and cæsium with some potassium is precipitated as silicomolybdate from an acid solution of the once recrystallised carnallite. The molybdenum is removed by volatilisation as oxychloride in a current of hydrogen chloride. If in the first instance only enough silicomolybdic acid is added to precipitate 10% of the total rubidium and cæsium, the precipitate contains all the cæsium and practically no potassium; the remaining rubidium is thrown down by a second addition of silicomolybdic acid. By carrying out the silicomolybdate precipitation thus in two stages, the separation of pure cæsium and rubidium preparations is greatly facilitated.

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[51] J. D'Ans and J. Löffler, *Ber.*, 1930, **63**, [*B*], 1446; *A.*, 1005.

[52] *J.*, 1930, 1473; *A.*, 1136.

[53] A. Ferrari and C. Colla, *Atti R. Accad. Lincei*, 1930, [vi], **11**, 755; *A.*, 1388.

[54] R. Scholder and C. F. Linström, *Ber.*, 1930, **63**, [*B*], 2828; *A.*, 1931, 66.

[55] T. R. Briggs and W. F. Geigle, *J. Physical Chem.*, 1930, **34**, 2250; *A.*, 1521.

[56] T. R. Briggs, J. A. Greenwald, and J. N. Leonard, *ibid.*, p. 1951; *A.*, 1374; T. R. Briggs, *ibid.*, p. 2260; *A.*, 1522.

[57] G. Jander and H. Faber, *Z. anorg. Chem.*, 1929, **179**, 321; *B.*, 1929, 641; G. Jander and F. Busch, *ibid.*, 1930, **187**, 165; **194**, 38; *A.*, 1930, 435; 1931, 49.

The pentaborates of potassium, rubidium, and cæsium, $5B_2O_3,M_2O,8H_2O$, form isomorphous (orthorhombic) crystals.[58]

With the exception of the lithium compound, nitrides of the alkali metals are difficult to prepare, and in no case had it been demonstrated that they are of the type M_3N. Under the influence of the glow discharge, the alkali metals and their amalgams take up nitrogen. When this occurs at room temperature the compound formed is practically entirely azide,[59] but at higher temperatures and with excess of alkali metal, nitride formation is favoured.[60] A small amount of nitride is formed during the thermal decomposition of alkali azides, and it has now been shown that rubidium and cæsium nitrides formed in this way have the formulæ Rb_3N and Cs_3N.[61]

H. J. S. King has prepared a large number of ammines of cupric salts of monobasic acids, including some of cupric iodide.[61a] The ammines and ammine hydrates of cupric selenate [62] and selenite [63] have been prepared and examined, and a large number of alkali cupric carbonates are stated to exist.[64]

Some interesting studies of the dehydration of single crystals of copper sulphate pentahydrate have been made by W. E. Garner and M. G. Tanner.[65]

The solubilities of silver chloride, bromide, and iodide in methyl and ethyl alcohols have been determined by an electrochemical method,[66] and it is suggested that the solubility of silver iodide in acetone solutions of sodium iodide is due to the formation of an anion $[I(IAg)_3]'$. Several sodium argentothiosulphates and the acid $H(AgS_2O_3),H_2O$ have been prepared.[67]

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[58] A. P. Rollet and L. Andès, *Compt. rend.*, 1930, **191**, 567; *A.*, 1386.

[59] W. Moldenhauer and H. Möttig, *Ber.*, 1929, **62**, [*B*], 1954; *A.*, 1929, 1247.

[60] H. Wattenberg, *ibid.*, 1930, **63**, [*B*], 1667; *A.*, 1137.

[61] K. Clusius, *Z. anorg. Chem.*, 1930, **194**, 47; *A.*, 1931, 50.

[61a] *J.*, 1930, 2307; *A.*, 1536.

[62] L. C. Hurd and V. Lenher, *J. Amer. Chem. Soc.*, 1930, **52**, 3857; *A.*, 1536.

[63] L. C. Hurd, G. I. Kemmerer, and V. W. Meloche, *ibid.*, p. 3881; *A.*, 1536.

[64] A. Cocosinschi, *Bull. Acad. Sci. Roumaine*, 1929, **12**, 19; *A.*, 307.

[65] *J.*, 1930, 47; *A.*, 428.

[66] F. K. V. Koch, *ibid.*, pp. 1551, 2385; *A.*, 1107, 1511.

[67] H. Baines, *ibid.*, 1929, 2763; *A.*, 175.

Cryoscopic measurements of the molecular weight of gold dissolved in various metals show that it is unimolecular between 400° and 1550°.[68]

A number of triple bromides of rubidium, tervalent gold, and copper, cadmium, mercury, thallium, bismuth, or antimony have been prepared and their properties described.[69]

Aurous chloride carbonyl is formed quantitatively from aurous chloride and carbon monoxide in benzene at 15° or from auric chloride in tetrachloroethylene at 130—140°. It has *M*, 223 (calc., 260) in freezing benzene, and dissociates in a vacuum or in hot solvents to give pure aurous chloride. It reacts with nitrogenous bases, the carbonyl group being displaced by 1 mol. of base.[70]

Group II.

A question, which has nowadays lost the interest it once had, has been revived by P. Pfeiffer, T. Fleitmann, and R. Hansen [71] in a discussion as to whether beryllium and magnesium are better classed with zinc and cadmium or with calcium, strontium, and barium. The question is considered with reference to the degree of hydration and ammoniation of the salts of various aromatic sulphonic acids, and it is concluded that beryllium and magnesium are better classed with zinc and cadmium. A number of such salts of nickel, copper, zinc, and cadmium were also made. The beryllium *p*-toluenesulphonate and β-naphthalenesulphonate have six molecules of water of crystallisation, although the α-naphthalenesulphonate only has four and the ammines never have more than 4 mols. of ammonia. The first two salts are considered to be the first certain cases of salts containing 6-co-ordinated beryllium. It is plain that alternative explanations are possible, however.

Pure beryllium can be deposited electrolytically from solutions of its anhydrous salts in liquid ammonia.[72]

The molecular weight of magnesium dissolved in other metals corresponds to a monatomic molecule above 700°.[73] Anhydrous magnesium perchlorate [74] and barium oxide [75] have been recommended as drying agents. It is concluded from spectroscopic observations that in a magnesium arc burning in water vapour there is not merely displacement of hydrogen by the magnesium, but also a second reaction resulting in the simultaneous formation of magnesium oxide and hydride.[76] In continuation of his studies of oxide hydrates, Hüttig has published papers dealing with the oxides of beryllium,[77] magnesium,[78] calcium,[79] strontium,[80] and cadmium.[81] A number of points connected with the technique of such investigations, such as the measurement of water-vapour pressure of hydroxide gels, have been discussed.[82] It has been shown that when due attention is paid to the preparation of pure products, the hydrated peroxides of calcium, strontium, and barium all correspond to the formula $MO_2,8H_2O$.[83] Several papers have been published on magnesium carbonates,[84] and it is said that a very unstable monohydrate of calcium carbonate exists besides the much more stable hexahydrate.[85] The calcium aluminates have been investigated by several workers.[86] The action of nitrogen peroxide on calcium carbonate, lime, and calcium phosphate has been investigated, and that of sulphur dioxide on calcium carbonate and phosphate. The use of calcium carbonate in the recovery of nitrous gases is suggested.[87] The solubilities of several radium salts have been determined.[88]

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[68] A. Jouniaux, *Bull. Soc. chim.*, 1930, [iv], **47**, 682; *A.*, 1243.

[69] E. S. Burkser, S. G. Rublov, and A. M. Scharnovsky, *Z. anorg. Chem.*, 1929, **185**, 144; *A.*, 175.

[70] M. S. Kharasch and H. S. Isbell, *J. Amer. Chem. Soc.*, 1930, **52**, 2919; *A.*, 1277.

[71] *J. pr. Chem.*, 1930, **128**, 47; *A.*, 1536; P. Pfeiffer, T. Fleitmann, and T. Inoue, *Z. anorg. Chem.*, 1930, **192**, 346; *A.*, 1390.

[72] H. S. Booth and G. G. Torrey, *J. Amer. Chem. Soc.*, 1930, **52**, 2581; *A.*, 1004.

[73] A. Jouniaux, *Bull. Soc. chim.*, 1930, [iv], **47**, 686; *A.*, 1243.

[74] S. Lenher and G. B. Taylor, *Ind. Eng. Chem.* (*Anal.*), 1930, **2**, 58; *A.*, 568.

[75] H. S. Booth and L. H. McIntyre, *ibid.*, p. 12; *A.*, 568.

The supposed allotropic changes undergone by zinc and bismuth are really due to impurities, but thallium and cobalt undergo reversible changes respectively at 225·2° and at 444° and 1128°.[89]

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[76] G. Piccardi, *Gazzetta*, 1930, **60**, 337; *A.*, 1006.

[77] G. F. Hüttig and K. Toischer, *Z. anorg. Chem.*, 1930, **190**, 364; *A.*, 996.

[78] G. F. Hüttig and W. Frankenstein, *ibid.*, **185**, 413; *A.*, 293.

[79] G. F. Hüttig, A. Arbes, Z. Herrmann, and C. Slonim, *ibid.*, **191**, 161; *A.*, 1372.

[80] G. F. Hüttig and A. Arbes, *ibid.*, **192**, 225; A., 1373.

[81] G. F. Hüttig and R. Mytyzek, *ibid.*, **190**, 353; *A.*, 996.

[82] G. F. Hüttig and K. Toischer, *Kolloidchem. Beih.*, 1930, **31**, 347; *A.*, 1373.

[83] C. Nogareda, *Anal. Fis. Quim.*, 1930, **28**, 461; *A.*, 1006.

[84] H. Menzel, A. Brückner, and H. Schulz, *Z. Elektrochem.*, 1930, **36**, 188; *A.*, 718; H. Menzel and A. Brückner, *ibid.*, p. 63; *A.*, 435; G. F. Hüttig and W. Frankenstein, *Z. anorg. Chem.*, 1930, **185**, 413; *A.*, 293.

[85] F. Krauss and W. Schriever, *Z. anorg Chem.*, 1930, **188**, 259; *A.*, 718.

[86] S. Nagai and R. Naito, *J. Soc. Chem. Ind. Japan*, 1930, **33**, 17; A., 436; T. Thorvaldson and N. S. Grace, *Canad. J. Res.*, 1929, **1**, 36; *A.*, 436; G. Assarson, *Z. anorg. Chem.*, 1930, **191**, 333; *A.*, 1262; A. Travers and J. Sehnoutka, *Ann. Chim.*, 1930, [x], **13**, 255; *A.*, 872.

[87] E. Briner, J. P. Lugrin, and R. Monnier, *Helv. Chim. Acta*, 1930, **13**, 64, 76, 80; *A.*, 436.

[88] O. Erbacher, *Ber.*, 1930, **63**, [*B*], 141; *A.*, 406.

[89] A. Schulze, *Z. Metallk.*, 1930, **22**, 194, 308; *B.*, 1073; *Z. tech. Physik*, 1930, **11**, 16; *A.*, 1355.

Zinc hydroxide exists in five different crystalline forms[90] and a number of well-defined basic salts are formed by prolonged action of the hydroxide or oxide on solutions of zinc salts.[91] The complex nature of the curious fractional hydrates of zinc chloride is indicated by the solid solutions containing cobalt chloride which they form.[92] The degree of association of cadmium iodide and of mercuric chloride and bromide in acetone solution has been determined, as also the solubilities, which are lower than those reported by previous workers.[93]

The solubilities of cadmium in its molten halides, of mercury in mercuric iodide, and of zinc and magnesium in their respective chlorides have been determined. The solution of cadmium in molten cadmium chloride is due to formation of a subchloride which is only stable whilst the mixture is liquid.[94]

The conditions under which tetramminomercuric salts can be formed have been discussed, and a number of these salts, as well as some diammino-salts, have been prepared.[95] The action of ammonia on the compounds $HgCl_2,2NH_3$ and $HgBr_2,2NH_3$ has been studied, and the compounds Hg_2NBr and Hg_2NCl,H_2O prepared.[96] Unlike most bi- and ter-valent metals, mercury and bismuth do not form inner complex phenoxides with 8-hydroxyquinoline; various compounds are formed, however, and a number have been prepared, such as those formulated as $[HgCl_2(C_9H_8ON)]Cl$ and $BiCl_3(C_9H_7ON,HCl)_2,EtOH$.[97]

Group III.

F. Faltis[98] has put forward views with regard to the structure of the boron hydrides involving cyclic structures for the higher members. E. Wiberg[99] considers that boron is quinquevalent towards hydrogen and is so in B_2H_6, the two boron atoms being doubly bound. Aluminium and cerium borides on treatment with acids give small yields of the same boron hydrides as are furnished by magnesium boride.[1] Beryllium boride has the advantage over magnesium boride for the preparation of boron hydrides because it furnishes a gas free from silanes which are troublesome to remove.[2] B_4H_{10} has now been prepared in quantity, and its reactions with hydrogen chloride, sodium amalgam, and ammonia studied in detail.[3]

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[90] W. Feitknecht, *Helv. Chim. Acta*, 1930, **13**, 314; *A.*, 700.

[91] *Idem*, *ibid.*, p. 22; *A.*, 436.

[92] H. Bassett and H. H. Croucher, *J.*, 1930, 784; *A.*, 1251.

[93] C. Zapata y Zapata, *Anal. Fis. Quim.*, 1930, **28**, 603; *A.*, 1362.

[94] G. von Hevesy and E. Löwenstein, *Z. anorg. Chem.*, 1930, **187**, 266; *A.*, 437.

[95] E. Weitz, K. Blasberg, and E. Wernicke, *ibid.*, **188**, 344; *A.*, 719.

[96] M. François, *Compt. rend.*, 1930, **190**, 125, 744, 1507; *Bull. Soc. chim.*, 1930, [iv], **47**, 165, 559, 825; *A.*, 307, 557, 1006, 1138, 1262.

[97] L. Dede and W. Hessler, *Z. anorg. Chem.*, 1930, **188**, 325; *A.*, 719.

[98] *Ibid.*, **187**, 369; *A.*, 524.

[99] *Ibid.*, p. 362; *A.*, 524.

[1] B. D. Steele and J. E. Mills, *J.*, 1930, 74; *A.*, 437.

Phenylborine, BH_2Ph, and boronbenzene, BPh : BPh, are described by E. Pace.[4] The distillation of boric acid in steam has been studied by G. Banchi and M. Giannotti.[5] Structures for the various boric acids and borates have been put forward which fall into line with those now customary for poly- and hetero-poly-acids, with a central boron atom to which boric acid residues are co-ordinated.[6] They seem preferable to the long-chain formulæ proposed by E. Wiberg.[7] By electrolysis of fused borates and borate–fluoride mixtures, amorphous boron has been obtained as well as borides of many metals of Groups III, IV, V, VI, and VII.[8]

Fluoroborates other than those corresponding with the formula MBF_4 are said to exist.[9]

The changes undergone by hydrated alumina during dehydration and heating have been followed by *X*-ray examination.[10]

A number of spinels, $M^{II}M_2^{III}O_4$ (M^{II} = Cu,Mg,Zn,Mn; M^{III} = Al,Fe,Cr), have been prepared by precipitation of the mixed oxides or evaporation of mixed nitrates and calcination at about 800° in each case.[11] Anhydrous aluminium alums of the general formula $MAl(SO_4)_2$ are precipitated by addition of hot concentrated sulphuric acid to the hot concentrated mixed sulphate solutions.[12]

Gallium tribromide, tri-iodide,[13] and trisulphide[14] have been prepared directly from the elements. By reduction of Ga_2S_3 with hydrogen GaS is obtained, and on being heated in a high vacuum, this breaks up into Ga_2S and Ga_2S_3.

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[2] A. Stock, E. Wiberg, and H. Martini, *Z. anorg. Chem.*, 1930, **188**, 32; *A.*, 720.

[3] *Idem*, *Ber.*, 1930, [*B*], **63**, 2927; *A.*, 1931, 50.

[4] *Atti R. Accad. Lincei*, 1929, [vi], **10**, 193; *A.*, 354.

[5] *Ann. Chim. Appl.*, 1930, **20**, 271, 286, 296; *A.*, 1361.

[6] F. L. Hahn, *Z. anorg. Chem.*, 1930, **193**, 316; *A.*, 1502.

[7] *Ibid.*, **191**, 43; *A.*, 1096.

[8] L. Andrieux, *Ann. Chim.*, 1929, [x], **12**, 423; *A.*, 305.

[9] A. Travers and L. Malaprade, *Bull. Soc. chim.*, 1930, [iv], **47**, 788; *A.*, 1261.

[10] W. Biltz, A. Lemke, and K. Meisel, *Z. anorg. Chem.*, 1930, **186**, 373; *A.*, 399; N. Parravano and E. Onorato, *Atti R. Accad. Lincei*, 1929, [vi], **10**, 475; *A.*, 437; G. F. Hüttig and O. Kostelitz, *Z. anorg. Chem.*, 1930, **187**, 1; *A.*, 543.

[11] L. Passerini, *Gazzetta*, 1930, **60**, 389; *A.*, 1007.

[12] N. Schischkin, *Z. anorg. Chem.*, 1930, **189**, 289; *A.*, 720.

[13] W. C. Johnson and J. B. Parsons, *J. Physical Chem.*, 1930, **34**, 1210; *A.*, 874.

[14] A. Brukl and G. Ortner, *Naturwiss.*, 1930, **18**, 393; *A.*, 720; *Monatsh.*, 1930, **56**, 358; *A.*, 1537; W. C. Johnson and B. Warren, *Naturwiss.*, 1930, **18**, 666; *A.*, 1138.

Thallic oxide does not appear to form any definite hydrate.[15]

A number of alkali ceric oxalates have been described.[16]

Europium may be separated from samarium and gadolinium as $EuSO_4$, which is insoluble in dilute acid, by electrolytic reduction in presence of sulphate.[17] Ytterbium can be similarly separated, practically quantitatively, in one operation as $YbSO_4,xH_2O$ of 98% purity, from the pink yttria-group oxides containing yttrium and erbium with small amounts of thulium and ytterbium. The $Yb^{\cdot\cdot}$ ion is green.[18]

Samarium di-iodide is best prepared by thermal dissociation of the tri-iodide in a high vacuum. On strong heating in a vacuum, $SmCl_2$ undergoes the type of decomposition characteristic of lower-valency compounds to give metal and $SmCl_3$.[19]

The sulphides of a large number of rare-earth metals have been prepared by heating the chloride or sulphate in a current of hydrogen sulphide. They fall into two groups with different crystal lattices and different colours.[20] Praseodymium forms two different double sulphates with ammonium sulphate.[21] The solubilities of several rare-earth salts have been determined.[22]

Group IV.

Measurements of parachors and dipole moments have furnished important evidence for the structure of the compounds of bivalent carbon, which are shown to be best formulated thus: Carbon monoxide, $\mathrm{C}\overset{\leftarrow}{\equiv}\mathrm{O}$; the *iso*cyanides, $\mathrm{R{-}N}\overset{\rightarrow}{\equiv}\mathrm{C}$.[23]

Purified wood charcoal reacts spontaneously with fluorine at the ordinary temperature, a variety of carbon fluorides being formed. The chemical and physical properties of the tetrafluoride have been examined.[24]

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[15] G. F. Hüttig and R. Mytyzek, *Z. anorg. Chem.*, 1930, **192**, 187; *A.*, 1373.

[16] J. Štěrba-Böhm and A. Písaříček, *J. Czech. Chem. Comm.*, 1930, **2**, 244; A., 1007.

[17] L. F. Yntema, *J. Amer. Chem. Soc.*, 1930, **52**, 2782; *A.*, 1134.

[18] R. W. Ball and L. F. Yntema, *ibid.*, p. 4264; *A.*, 1931, 51.

[19] G. Jantsch, *Naturwiss.*, 1930, **18**, 155; *A.*, 437; G. Jantsch and N. Skalla, *Z. anorg. Chem.*, 1930, **193**, 391; *A.*, 1931, 51.

[20] W. Klemm, K. Meisel, and H. U. von Vogel, *Z. anorg. Chem.*, 1930, **190**, 123; *A.*, 874.

[21] F. Zambonini and S. Restaino, *Atti R. Accad. Lincei*, 1930, [vi], **11**, 774; *A.*, 1387.

[22] K. S. Jackson and G. Rienäcker, *J.*, 1930, 1687; *A.*, 1107; J. A. N. Friend, *ibid.*, pp. 1633, 1903; *A.*, 1107, 1246.

[23] D. L. Hammick, R. C. A. New, N. V. Sidgwick, and L. E. Sutton, *ibid.*, p. 1876; *A.*, 1239; H. Lindemann and L. Wiegrebe, *Ber.*, 1930, **63**, [*B*], 1650; *A.*, 1171.

The reaction $COS + 2NH_3 = CO(NH_2)_2 + H_2S$ affords a more suitable method for the manufacture of carbamide than the older process using ammonia and carbon dioxide.[25]

Carbonyl chloride is produced when carbon monoxide is passed over the heated chlorides of ruthenium, platinum, and gold, but not of rhodium, palladium, or osmium.[26]

The hydrolysis of the cyanides of sulphur, selenium, tellurium, and phosphorus has been studied,[27] their molecular volumes measured,[28] and the mobility of the OCN, SCN, SeCN, $N(CN)_2$, $C(CN)_3$, and N_3 ions determined.[29]

Vapour-pressure curves are taken to indicate the existence of five definite silica hydrates.[30] Very slow potentiometric titration of silicate solutions has been tried as a means of studying the silicic acids, but without very definite results.[31]

The attack of silica by hydrofluoric acid is not primarily dependent upon the concentration of the latter but upon that of the HF_2' ion, and is directly proportional to it when the total ionic concentration is high.[31a]

Anhydrous titanium di- and tri-bromides have been prepared for the first time,[32] the latter by reduction of the tetrabromide at a red heat with hydrogen. On being heated at 400° in an atmosphere of hydrogen, the tribromide breaks up in accordance with the equation $2TiBr_3 \longrightarrow TiBr_2 + TiBr_4$; the dibromide itself undergoes the reaction $2TiBr_2 \longrightarrow Ti + TiBr_4$, but only slowly at 650°. Both the lower bromides react with hydrogen bromide to form the tetrabromide, and the reaction is rapid above 350°. Titanium metal reacts with hydrogen bromide above 300°, and the lower the temperature the more di- and tri-bromide are formed, which is similar to what was found for the reaction of hydrogen bromide with silicon.[33]

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[24] O. Ruff and R. Keim, *Z. anorg. Chem.*, 1930, **192**, 249; *A.*, 1387; P. Lebeau and A. Damiens, *Compt. rend.*, 1930, **191**, 939; *A.*, 1931, 52.

[25] A. Klemenc, *Z. anorg. Chem.*, 1930, **191**, 246; *A.*, 1387.

[26] W. Manchot and G. Lehmann, *Ber.*, 1930, **63**, [*B*], 1221; *A.*, 875.

[27] L. Birckenbach, K. Huttner, W. Stein, and F. Ensslin, *Z. anorg. Chem.*, 1930, **190**, 1; *A.*, 876.

[28] K. Huttner and S. Knappe, *ibid.*, p. 27; *A.*, 876.

[29] L. Birckenbach and K. Huttner, *ibid.*, p. 38; *A.*, 876.

[30] P. A. Thiessen and O. Koerner, *Z. anorg. Chem.*, 1930, **189**, 168, 174; *A.*, 720.

[31] W. D. Treadwell and W. Wieland, *Helv. Chim. Acta*, 1930, **13**, 842; *A.*, 1537.

[31a] W. G. Palmer, *J.*, 1930, 1656; *A.*, 1133.

[32] R. C. Young and W. C. Schumb, *J. Amer. Chem. Soc.*, 1930, **52**, 4233; *A.*, 1931, 51.

[33] *Idem, ibid.*, p. 1464; *A.*, 720.

The existence of various zirconates has been demonstrated by means of fusion diagrams.[34]

Pure zirconium and hafnium metals have been prepared by thermal decomposition of the iodides.[35] The melting point and density of metallic hafnium are about 2500° Abs. and 13·31 respectively.

The precautions necessary to ensure the absence of impurities when preparing pure hafnium salts have been described.[36] The solubilities of the oxyfluorides and oxybromides of zirconium and hafnium in hydrofluoric and hydrobromic acid solutions have been determined.[37]

The lowest hydrate of thorium nitrate is $Th(NO_3)_4,2H_2O$ but thoryl nitrate, $ThO(NO_3)_2,\frac{1}{2}H_2O$, can be obtained by desiccation of thorium nitrate in a current of air, carrying nitric acid vapour, above 110°.[38]

Germanium monohydride, a dark brown powder, is formed by the action of cold water on sodium germanide.[39] Amorphous and crystalline germanium monoxide and monosulphide have been described,[40] as also several sulpho- and per-germanates,[41] and several phenyl germanium compounds.[42] Germanium imide, germanam (Ge_2N_3H), and germanium nitride are formed when ammonia acts upon germanium tetrachloride.[43] R. Schwarz and H. Giese show that germanium tetrachloride forms no compound with hydrogen chloride corresponding to H_2GeF_6. In this respect germanium is like silicon and unlike tin. They have also prepared 12-molybdogermanic acid, $H_8[Ge(Mo_2O_7)_6]$, and the corresponding tungsten compound and their guanidinium salts.[44] Several salts of the 12-tungstogermanic acid have been described.[44a]

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[34] H. von Wartenberg and H. Werth, *Z. anorg. Chem.*, 1930, **190**, 178; *A.*, 847.

[35] J. H. de Boer and J. D. Fast, *Z. anorg. Chem.*, 1930, **187**, 177, 193; *A.*, 437.

[36] J. H. de Boer and J. Broos, *ibid.*, p. 190; *A.*, 438.

[37] G. von Hevesy and O. H. Wagner, *ibid.*, **191**, 194; *A.*, 1362.

[38] E. Chauvenet and Mme. Souteyrand-Franck, *Bull. Soc. chim.*, 1930, [iv], **47**, 1128; *A.*, 1538.

[39] L. M. Dennis and N. A. Skow, *J. Amer. Chem. Soc.*, 1930, **52**, 2369; *A.*, 1007.

[40] L. M. Dennis and R. E. Hulse, *ibid.*, p. 3553; *A.*, 1388; W. Pugh, *J.*, 1930, 2369; *A.*, 1537.

[41] R. Schwarz and H. Giese, *Ber.*, 1930, **63**, [*B*], 778; *A.*, 720.

[42] C. A. Kraus and C. B. Wooster, *J. Amer. Chem. Soc.*, 1930, **52**, 372; *A.*, 354; C. A. Kraus and C. L. Brown, *ibid.*, p. 4031; *A.*, 1602.

[43] R. Schwarz and P. W. Schenk, *Ber.*, 1930, **63**, [*B*], 296; *A.*, 437.

[44] *Ibid.*, p. 2428; *A.*, 1537.

[44a] A. Brukl, *Monatsh.*, 1930, **56**, 179; *A.*, 1538.

It is doubtful whether octammines of tin have been prepared.[45] Products supposed to be such were found to correspond to the formula $[Sn,xNH_3,yH_2O]I_4$, where $x + y$ was approximately equal to 8.

Lead perchlorate and its mono- and tri-hydrates have been made. The anhydrous salt is extremely soluble in water and is also soluble in organic solvents.[45a] Crystalline and hydrated lead dioxides have been prepared, and the dehydration curves of the latter examined.[46] A dihydrate of lead oxalate is precipitated at 0° and it is shown that lead oxalate (and manganous oxalate) are probably complex.[47]

Group V.

Attempts to separate nitrogen into para- and ortho-forms similar to those of hydrogen have not been successful,[48] although Smits considers that he has evidence which indicates the complexity of nitrogen.[49]

Further work has been published on the constituents of active nitrogen [50] and on the decay of its afterglow.[51] The amount of active nitrogen present can be determined by shaking the gas with mercury at room temperature and estimating the ammonia formed by treatment of the product with 2·5% sodium hydroxide. The most suitable phosphor for use with active nitrogen is boron nitride activated with carbon.[52]

Some hydrazine is formed when a mixture of ammonia and nitrogen is passed over nickel gauze at 340—355° or during the catalytic oxidation of ammonia by fine copper gauze at 340—400° at low pressures, the ammonia being in excess. It can also be obtained by burning oxygen in ammonia.[53] Reduction of nitric oxide by platinised platinum in dilute hydrochloric acid produces small amounts of hydroxylamine and ammonia.[54] Nitrosyl perchlorate and nitrosylsulphuric acid are considered to be salts,[55] $[NO]^{\cdot}[ClO_4]'$ and $[NO]^{\cdot}[HO{\cdot}SO_3]'$. The additive compounds of phosphine and the tetrahalides of the elements of Group IV have been examined.[56]

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[45] A. J. Cooper and W. Wardlaw, *J.*, 1930, 1141; *A.*, 874.

[45a] H. H. Willard and J. L. Kassner, *J. Amer. Chem. Soc.*, 1930, **52**, 2391; *A.*, 1007.

[46] A. Simon, *Z. anorg. Chem.*, 1930, **185**, 280, 300; *A.*, 289, 308.

[47] R. Scholder and C. F. Linström, *Ber.*, 1930, **63**, [*B*], 2831; *A.*, 1931, 66.

[48] E. Justi, *Naturwiss.*, 1930, **18**, 227, 393; *A.*, 524, 721; P. Harteck and H. W. Schmidt, *ibid.*, p. 282; *A.*, 557.

[49] A. Smits and J. de Gruyter, *Proc. K. Akad. Wetensch. Amsterdam*, 1930, **33**, 86; *Physikal. Z.*, 1930, **31**, 435; *A.*, 659; A. Smits, H. Gerding, and (Miss) W. Hertogh, *Proc. K. Akad. Wetensch. Amsterdam*, 1930, **33**, 526; *Physikal. Z.*, 1930, **31**, 768; *A.*, 1096.

[50] Z. Bay and W. Steiner, *Z. physikal. Chem.*, 1930, [*B*], **9**, 93; *A.*, 1087.

[51] E. J. B. Willey, *J.*, 1930, 336, 1146; *A.*, 524, 838.

[52] E. Tiede and H. Chomse, *Ber.*, 1930, **63**, [*B*], 1839; *A.*, 1139.

[53] K. A. Hofmann and J. Korpiun, *Ber.*, 1929, **62**, [*B*], 3000; *A.*, 171.

[54] A. J. Butterworth and J. R. Partington, *Trans. Faraday Soc.*, 1930, **26**, 144; *A.* 429.

An investigation of the oxidation of phosphorus by oxygen and by air, both alone and in presence of moisture and of substances inhibiting phosphorescence, has led to the conclusion that the oxidation has its seat in the gas phase and is autocatalysed by atomic oxygen.[57]

The vapour pressures of phosphoric oxide under various conditions of heating have been determined, and the results interpreted in terms of the author's theory of allotropy.[58] Diammonium amidopyrophosphate is formed by the action of gaseous ammonia on phosphoric oxide.[59]

The small amount of hexafluorophosphoric acid produced by the action of phosphoric oxide on aqueous hydrofluoric acid can be isolated as the nitron salt. A large number of salts of the acid have been prepared and described. The nitron salts of hexafluoroarsenate and hexafluoroantimonate have been prepared by evaporation of potassium dihydrogen arsenate or potassium pyroantimonate with hydrofluoric acid, followed by addition of ammonium and nitron acetates.[60]

The variations in the colour of arsenious sulphide are purely physical in nature.[61] L. W. McCay and W. Foster [62] showed that a very rapid current of hydrogen sulphide precipitates arsenic pentasulphide from solutions of arsenic acid after primary formation of monothioarsenic acid. This has been confirmed.[63] Pyroarsenic acid itself and a number of pyroarsenates have been prepared.[64] Some further work on explosive antimony has been published,[65] and a number of very complex chloroantimonates[66] and bromoantimonites[67] are said to be formed by methods given.

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[55] A. Hantzsch and K. Berger, *Z. anorg. Chem.*, 1930, **190**, 321; *A.*, 1007.

[56] R. Höltje, *ibid.*, p. 241; *A.*, 876.

[57] J. Tausz and H. Görlacher, *ibid.*, p. 95; *A.*, 876.

[58] A. Smits and H. W. Deinum, *Proc. K. Akad. Wetensch. Amsterdam*, 1930, **33**, 514, 619; *Z. physikal. Chem.*, 1930, **149**, 337; *A.*, 1096, 1372, 1251.

[59] A. Sanfourche, A. Hernette, and M. Fau, *Bull. Soc. chim.*, 1930, [iv], **47**, 273; *A.*, 557.

[60] W. Lange and E. Müller, *Ber.*, 1930, **63**, [*B*], 1058; *A.*, 877.

[61] H. B. Weiser, *J. Physical Chem.*, 1930, **34**, 1021; *A.*, 721.

[62] L. W. McCay, *Amer. Chem. J.*, 1888, **10**, 459; *Z. anal. Chem.*, 1888, **27**, 632; *A.*, 1889, ii, 15; L. W. McCay and W. Foster, *Ber.*, 1904, **37**, 573; *A.*, 1904, ii, 253; W. Foster, *J. Amer. Chem. Soc.*, 1916, **38**, 52; *A.*, 1916, ii, 246.

[63] F. Foerster, G. Pressprich, and W. Reuss, *Z. anorg. Chem.*, 1930, **188**, 90; *A.*, 721.

[64] A. Rosenheim and H. Antelmann, *ibid.*, **187**, 385; *A.*, 558; A. Rosenheim, *ibid.*, **193**, 73; *A.*, 1388.

[65] E. Cohen and C. C. Coffin, *Z. physikal. Chem.*, 1930, **149**, 417; *A.*, 1258; H. von Steinwehr and A. Schulze, *Z. Physik*, 1930, **63**, 815; *A.*, 1258.

The preparation and analysis of $K_2V(CN)_6$ has been described.[68] Vapour-pressure measurements have been carried out with the precipitated vanadic, niobic, and tantalic acids, but only with the first was there any indication of the existence of definite hydrates.[69] The isotherms and isobars of the system niobium–hydrogen are similar in form to those for vanadium and tantalum hydrides.[70] Borides of niobium and tantalum have been prepared,[71] and the reaction of tantalum pentoxide with hydrogen chloride has been investigated.[72]

It has been pointed out that element 91 (protoactinium) is chemically more like zirconium and thorium than like tantalum, and the carrier of this element in the residues from radium refining is zirconium phosphate and not tantalum pentoxide. A due appreciation of these facts facilitates the extraction of protoactinium, which occurs to the extent of about 0·6 mg. per g. of radium in uranium ores. Protoactinium (= ekatantalum) pentoxide is a heavy white powder, not acidic but definitely, though feebly, basic, soluble in fused sodium hydrogen sulphate, but not in fused sodium carbonate.[73]

Group VI.

The mean normal boiling point of oxygen is $-182{\cdot}97° \pm 0{\cdot}010°$.[74] The colour produced by the action of ozone on ammonia depends on the amount of water present and upon the temperature.[75] Ozone decomposes sodium perborate.[76] A still for producing conductivity water has been described which is claimed to be cheap, strong, compact, durable, and easy to erect and to work.[77]

Experiments have been described which suggest that S_μ is a gel. In agreement with this, it is found that the Tyndall effect is to be observed in pure molten sulphur.[78] The cryoscopic behaviour of a number of substances in molten sulphur has been investigated.[79] Very pure sulphur hexafluoride has been prepared, and its vapour pressure measured between —72° and — 45°. The b. p. (760 mm.) is — 63·8°, and the m. p. — 50·8° ± 0·2°.[80]

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[66] L. I. Sauciuc, *Bul. Soc. Chim. România*, 1930, **12**, 36; *A.*, 1388.

[67] A. C. Vournazos, *Z. anorg. Chem.*, 1930, **192**, 369; A., 1388.

[68] A. Yakimach, *Compt. rend.*, 1930, **191**, 789; *A.*, 1931, 52.

[69] G. F. Hüttig and A. König, *Z. anorg. Chem.*, 1930, **193**, 81, 93, 100; *A.*, 1538.

[70] H. Hagen and A. Sieverts, *ibid.*, **185**, 225; *A.*, 308.

[71] L. Andrieux, *Compt. rend.*, 1929, **189**, 1279; *A.*, 178.

[72] V. Spitzin and L. Kaschtanov, *J. Russ. Phys. Chem. Soc.*, 1930, **62**, 295; *A.*, 877.

[73] A. von Grosse, *Z. anorg. Chem.*, 1930, **186**, 38; *A.*, 515; *J. Amer. Chem. Soc.*, 1930, **52**, 1742; *A.*, 883.

[74] W. H. Keesom, (Miss) H. van der Horst, and (Miss) A. F. J. Jansen, *Proc. K. Akad. Wetensch. Amsterdam*, 1929, **32**, 1167; *A.*, 403.

[75] W. Manchot, *Ber.*, 1930, **63**, [*B*], 1225; *A.*, 877.

[76] F. Fichter and A. Goldach, *Helv. Chim. Acta*, 1930, **13**, 1200.

[77] J. M. Stuart and F. Wormwell, *J.*, 1930, 85; *A.*, 434.

The best conditions for the preparation of pure hydrogen disulphide have been described, and many of the physical constants of the compound determined;[81] its parachor (130·0) shows that the molecule contains no double or co-ordinated valency linkage. The f. p. curve of the system sulphur–hydrogen disulphide has no break corresponding with hydrogen trisulphide, so the latter compound appears not to be a molecular compound of sulphur and hydrogen disulphide.

The structure $M_2[SO_3{\cdot}SO]$ is proposed for the hyposulphites and is considered to agree with various decompositions and reactions which they undergo.[82] The reactions between thiosulphate and sulphurous acid have been studied in detail, and upon them have been based good methods for preparing not only solid *potassium* trithionate but also solid *sodium* or *ammonium* tetrathionate.[83] The PO_3F ion of the fluorophosphates can replace the SO_4 ion isomorphously and a number of fluorophosphates belonging to the ferrous ammonium sulphate group and to the alums have been prepared, as well as simple fluorophosphates.[84]

Solid hexabromoselenous acid slowly loses bromine with formation of selenium monobromide. It will then give colloidal selenium on treatment with water, but the pure acid dissolves in water without any such separation of selenium.[85] The preparation of pure selenium and tellurium tetrachlorides has been described, and many of their physical constants have been measured.[86] The parachors of a number of tellurium compounds now determined give a mean constant for tellurium of 79·4, which lies satisfactorily between the constants for iodine and antimony.[87]

The m. p. of tellurium purified by fractional distillation is 452·0°

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[78] D. L. Hammick and M. Zvegintzov, *J.*, 1930, 273; *A.*, 419.

[79] C. R. Platzmann, *Bull. Chem. Soc. Japan*, 1929, **4**, 235; 1930, **5**, 79; *A.*, 143, 558.

[80] W. C. Schumb and E. L. Gamble, *J. Amer. Chem. Soc.*, 1930, **52**, 4302; *A.*, 1931, 52.

[81] K. H. Butler and O. Maass, *ibid.*, p. 2184; *A.*, 1008.

[82] O. von Deines and G. Elstner, *Z. anorg. Chem.*, 1930, **191**, 340; *A.*, 1262.

[83] A. Kurtenacker and J. A. Ivanov, *ibid.*, **185**, 337; *A.*, 302; A. Kurtenacker and K. Matejka, *ibid.*, **193**, 367; *A.*, 1931, 52.

[84] P. C. Rây, *Nature*, 1930, **126**, 310; *A.*, 1351.

[85] J. Meyer and V. Wurm, *Z. anorg. Chem.*, 1930, **190**, 90; *A.*, 877.

[86] J. H. Simons, *J. Amer. Chem. Soc.*, 1930, **52**, 3483, 3488; *A.*, 1356.

[87] F. H. Burstall and S. Sugden, *J.*, 1930, 229; *A.*, 399.

(vac.) and is lowered in hydrogen and carbon dioxide by 0·15° and 0·2° respectively.[88]

A method for preparing telluric acid directly from finely powdered tellurium by oxidation with chloric acid has been described.[89]

Several mixed crystals of hexacarbamidochromic salts have been prepared, such as those of permanganate and perchlorate, permanganate and fluoroborate,[90] and numerous complex chromic compounds have been described,[91] of which a number of chromicyanides raise some interesting questions concerning the stability of polynuclear complexes which are important in connexion with other complex cyanides. A new type of red perchromate has been prepared as the calcium salt $Ca_3Cr_2O_{12},12H_2O$ by adding 30% hydrogen peroxide to a saturated calcium chromate solution at $-5°$.[92]

Hydrazine in strongly acid boiling solution reduces sexavalent to quinquevalent molybdenum. In feebly acid solutions, complexes containing both quinque- and sexa-valent molybdenum are produced.[93] By the interaction of molybdenum pentachloride and various organic solvents, a number of substances have been obtained which are formulated as derivatives of molybdenyl chloride, $MoOCl_3$, and of molybdenum tetrachloride.[94] Molybdenum-blue has a variable chemical composition. It is soluble in many organic solvents and, although it is a colloid, it is immediately extracted from its aqueous solutions when they are shaken with certain organic solvents.[94a] Molybdic, tungstic (and vanadic) acids have been studied by the methods of potentiometric and conductometric titration but, on the whole, the results are disappointing and not always easy to interpret.[95] *X*-Ray methods also have been applied to the tungstic acids.[95a] A large number of paratungstates and heteropolytungstates have been described.[96] With organic bases uranyl fluoride forms double salts of three different types, *viz.*, $M(UO_2)F_3,nH_2O$, $M(UO_2)_2F_5,nH_2O$, and $M(UO_2)_3F_7,nH_2O$.[97]

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[88] A. Šimek and B. Stehlík, *J. Czech. Chem. Comm.*, 1930, **2**, 304; *A.*, 986.

[89] J. Meyer and W. Franke, *Z. anorg. Chem.*, 1930, **193**, 191; *A.*, 1389.

[90] E. Wilke-Dörfurt and R. Pfau, *Z. Elektrochem.*, 1930, **36**, 118; *A.*, 722.

[91] R. Weinland and J. Lindner, *Z. anorg. Chem.*, 1930, **190**, 285; *A.*, 878; H. I. Schlesinger and (Miss) R. K. Worner, *J. Amer. Chem. Soc.*, 1929, **51**, 3520; *A.*, 178; H. I. Schlesinger and D. N. Rickles, *ibid.*, p. 3523; *A.*, 178; H. Reihlen and F. Kraut, *Annalen*, 1930, **478**, 219; *A.*, 586.

[92] J. A. Raynolds and J. H. Reedy, *J. Amer. Chem. Soc.*, 1930, **52**, 1851; *A.*, 873.

[93] W. F. Jakób and W. Kozłowski, *Rocz. Chem.*, 1929, **9**, 667; *A.*, 308.

[94] W. Wardlaw and H. W. Webb, *J.*, 1930, 2100; *A.*, 1389.

[94a] J. Duclaux and R. Titéica, *Rev. gén. Colloid.*, 1929, **7**, 289; *A.*, 289.

[95] H. T. S. Britton and W. L. German, *J.*, 1930, 1249, 2154; *A.*, 860, 1371; H. T. S. Britton and R. A. Robinson, *ibid.*, pp. 1261, 2328; *A.*, 860, 1522; G. Jander and W. Heukeshoven, *Z. anorg. Chem.*, 1930, **187**, 60; *A.*, 438.

[95a] A. M. Morley, *J.*, 1930, 1987; *A.*, 1262.

Group VII.

The b. p. of fluorine has been found to be 84·93° Abs., and its critical temperature and pressure are about 144° Abs. and 55 atmos. Its vapour pressure has been measured over the range 72—86° Abs.[98]

The solid compounds formed by the union of hydrogen fluoride with perchloric acid and with boron fluoride are regarded as acidium salts by A. Hantzsch [99] and formulated as $[FH_2]^{\cdot}ClO_4{}'$ and $[FH_2]^{\cdot}BF_4{}'$, and several reactions of hydrogen fluoride and hydrogen chloride are interpreted in terms of the above $[FH_2]^{\cdot}$ ion and the corresponding $[ClH_2]^{\cdot}$ ion. It has been shown that KF,3HF is a definite compound, and a convenient apparatus for preparing fluorine by the electrolysis of this compound in the fluid condition at 100° has been described, with full details of procedure.[1] A good deal of work has been done on oxygen difluoride, the existence of which is now well established. It is a colourless gas condensing to a yellow liquid, b. p. $-$ 146·5°, m. p. $-$ 223·8°, heat of formation $-$ 4·6 $\pm$ 2 kg.-cals.[2] The m. p. of nitrogen trifluoride was determined at the same time and found to be somewhat above $-$ 216·6°.[3] According to H. von Wartenberg and G. Klinkott [1] the heat of formation of oxygen difluoride is $-$ 11 kg.-cals.; these authors have examined the chemical reactions of the gas in some detail. With potassium iodide solution the reaction $F_2O + 4HI = 4I + 2HF + H_2O$ occurs, and this was made the basis of its estimation. Hydrobromic acid acts similarly, and so does hydrochloric acid, but very slowly. With alkali the much slower reaction $F_2O + 2NaOH = 2NaF + H_2O + O_2$ occurs—no fluoroxy-acids being formed. Benzene absorbs the gas quantitatively, quinol and benzoquinone being formed. Reducing agents such as sodium thiosulphate, stannous chloride, ferrous sulphate, and arsenious oxide absorb oxygen as well as the difluoride from mixtures containing both, but only slowly. The oxygen difluoride is always prepared by P.

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[96] A. Rosenheim, A. Wolff, J. E. Koch, and M. Siao, *Z. anorg. Chem.*, 1930, **193**, 47, 64; *A.*, 1389.

[97] F. Olsson, *ibid.*, **187**, 112; *A.*, 439.

[98] G. H. Cady and J. H. Hildebrand, *J. Amer. Chem. Soc.*, 1930, **52**, 3839; *A.*, 1508.

[99] *Ber.*, 1930, **63**, [*B*], 1789; *A.*, 1140.

[1] *Z. anorg. Chem.*, 1930, **193**, 409; *A.*, 1931, 42.

[2] O. Ruff and W. Menzel, *ibid.*, **190**, 257; *A.*, 877.

[3] O. Ruff and K. Clusius, *ibid.*, p. 267; *A.*, 986.

Lebeau and A. Damiens's[4] method of passing fluorine in a fine stream through weak sodium hydroxide solution. The oxidising action of fluorine on potassium hydrogen sulphate solution, on silver, stannous, ferrous, and cobaltous salts, and on titanic, vanadic, and molybdic acids has been studied by F. Fichter and A. Goldach.[5]

By distribution experiments between nitrobenzene and water and between benzene and water, it is shown that in both non-aqueous solvents the concentration of hydrogen chloride is proportional to its partial pressure, indicating absence of ionisation. Since the dielectric constants of nitrobenzene and benzene are 34 and 2·2 respectively, the ionisation of hydrochloric acid cannot be determined by the dielectric constant of the solvent. The vapour-pressure data for aqueous hydrochloric acid solutions indicate that only hydrated molecules of the hydrogen chloride are ionised, and that they exert a negligible partial pressure. It is the basic character of the water, not its high dielectric constant, which determines its capacity to cause ionisation.[6] The reactivities of various oxides at different temperatures towards hydrogen chloride and towards chlorine have been investigated.[7] The parachor of chlorine dioxide has been determined, and several possible structures of the molecule are considered.[8]

A new chlorine fluoride, ClF_3, has been prepared[9] by heating either chlorine or its monofluoride with excess of fluorine. It is a colourless gas forming a pale green liquid, b. p. 11°, and a white solid, m. p. — 83°. It is chemically extremely active. A new fluoride of iodine, IF_7, has also been obtained by heating a mixture of iodine pentachloride and fluorine at 270—300°. It also is very reactive chemically, and is colourless.[10]

The existence of bromine chloride has been confirmed by the nature of the products formed when mixtures of chlorine and bromine react with aliphatic diazo-compounds.[11] According to H. Lux,[12] it is an ochre-yellow solid, m. p. — 54°, which rapidly decomposes in the vapour phase.

According to F. A. Philbrick,[13] the behaviour of iodine mono-

[4] *Compt. rend.*, 1927, **185**, 652; 1929, **188**, 1253; *A.*, 1927, 1044; 1929, 779; *Ann. Reports*, 1929, **26**, 63.

[5] *Helv. Chim. Acta*, 1930, **13**, 99, 378, 713, 1200; *A.*, 435, 722, 1140, 1537.

[6] W. F. K. Wynne-Jones, *J.*, 1930, 1064; *A.*, 859.

[7] R. Wasmuht, *Z. angew. Chem.*, 1930, **43**, 98, 125; *A.*, 439; V. Spitzin, *Z. anorg. Chem.*, 1930, **189**, 337; *A.*, 874.

[8] G. H. Cheesman, *J.*, 1930, 35; *A.*, 278.

[9] O. Ruff and H. Krug, *Z. anorg. Chem.*, 1930, **190**, 270; *A.*, 878.

[10] *Idem, ibid.*, **193**, 176; *A.*, 1390.

[11] T. W. J. Taylor and L. A. Forscey, *J.*, 1930, 2272; *A.*, 1565.

[12] *Ber.*, 1930, **63**, [*B*], 1156; *A.*, 878.

[13] *J.*, 1930, 2254; *A.*, 1520.

chloride in hydrochloric acid solution indicates that it is ionised to I˙ and Cl′.

Small amounts of a volatile oxide of bromine, probably Br_2O, are formed by the action of bromine on specially prepared, and very reactive, mercuric oxide between 50° and 100°.[14]

Potassium iodide can be partly converted into iodate by heating in oxygen under pressure, and if the iodide is mixed with potassium hydroxide the oxidation takes place still more readily, some periodate also being formed.[15]

The change of pink manganese sulphide into the orange and the green form occurs much more slowly if ammonium sulphide is used for precipitation instead of ammonium hydrogen sulphide and the addition of ammonia before that of its sulphide hinders the change very greatly. The green form is crystalline, but the other two are amorphous.[16]

Two series of complex manganifluorides have been obtained, *viz.*, $MMnF_4,nH_2O$ and M_2MnF_5, where M is an organic base. The former represents a new type, whilst the latter corresponds to the alkali manganifluorides.[17]

Manganese dioxide may be prepared from any lower oxide by direct oxidation with oxygen; by using sodium hydroxide as catalyst at 400—500°, a product containing 50—95% MnO_2 may be obtained.[18] $K_4Mn(CN)_8$ may be prepared by the addition of a saturated solution of potassium permanganate to an 80% solution of potassium cyanide until red acicular crystals are produced.[19]

Some new perchlorates and permanganates have been described, as well as a number of fluorosulphonates which are isomorphous with them.[20]

One hears no more of masurium nowadays, but rhenium is thoroughly well established among the elements. Very pure potassium per-rhenate can, in fact, now be obtained commercially from the " Vereinigten Fabriken zu Leopoldshall." Its technical preparation has been described by W. Feit.[21]

The formation of per-rhenate occurs so extremely easily that the preparation of compounds of the lower oxidation stages is very difficult. It has been shown that zinc and hydrochloric acid reduce per-rhenate through the various intermediate stages to metal, with the possibility of halting at these stages. Sodium amalgam and hydrazine both reduce it to metal, but in each case some admixture of lower oxides is present.[22] The electrical conductivity of potassium per-rhenate for concentrations between 0·04 and 0·0005 g.-mol. per litre has been determined at 18°, 25°, 30°, and 40°.[23] From weakly acid solutions soluble per-rhenates can be precipitated and estimated quantitatively by means of "nitron." [24]

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[14] E. Zintl and G. Rienäcker, *Ber.*, 1930, **63**, [*B*], 1098; *A.*, 878.

[15] F. A. Henglein and L. Teichmann, *Z. anorg. Chem.*, 1930, **188**, 138; A., 722.

[16] G. Landesen and M. Reistal, *ibid.*, **193**, 277; *A.*, 1539.

[17] F. Olsson, *ibid.*, **187**, 313; *A.*, 588.

[18] Y. Kato and T. Matsuhashi, *J. Soc. Chem. Ind. Japan*, 1929, **32**, 313 B, 315 B; *A.*, 1930, 308.

[19] A. Yakimach, *Compt. rend.*, 1930, **190**, 681; *A.*, 558.

[20] E. Wilke-Dörfurt, G. Balz, and A. Weinhardt, *Z. anorg. Chem.*, 1930, **185**, 417; *A.*, 308.

[21] *Z. angew. Chem.*, 1930, **43**, 459; *B.*, 822.

Group VIII.

The conditions under which iron reacts with carbon monoxide to form oxide, carbide, or graphite have been examined,[25] as have those necessary for the oxidation of ferrous hydroxide to ferrous ferrite rather than to ferric hydroxide.[26] Different forms of ferric hydroxide, γ- and α-, result according as ferrous ferrite is or is not an intermediate stage.[27] The results of recent work leave it doubtful what hydrates of ferric oxide actually exist.[28] The action of iron at high temperatures on hydrogen sulphide, hydrogen selenide, and carbon disulphide has been examined,[29] and a full investigation has been made of the reaction $FeS_2 \rightleftharpoons FeS + S$.[30] It has been shown that carbonyl groups in iron pentacarbonyl can be replaced by various amines, and a number of the compounds so obtained are described.[31] Several compounds of metal carbonyls with iron halides have been prepared, and the space occupied by carbon monoxide in various complex metal compounds has been estimated.[32] Iron tetracarbonyl, prepared by the action of alkali alkoxide on iron pentacarbonyl, has been shown to be $[Fe(CO)_4]_3$. Details of many of its reactions and derivatives are given.[33]

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[22] F. Krauss and H. Steinfeld, *Z. anorg. Chem.*, 1930, **193**, 385; *A.*, 1931, 53.

[23] N. A. Puschin and P. S. Tutundžić, *ibid.*, p. 420; *A.*, 1931, 43.

[24] W. Geilmann and A. Voigt, *ibid.*, p. 311; *A.*, 1547.

[25] V. Hofmann and E. Groll, *ibid.*, **191**, 414; *A.*, 1263.

[26] C. Sandonnini, *Gazzetta*, 1930, **60**, 321; *A.*, 878.

[27] G. Schikorr, *Z. anorg. Chem.*, 1930, **191**, 322; *A.*, 1263.

[28] P. A. Thiessen and R. Köppen, *Z. anorg. Chem.*, 1930, **189**, 113; *A.*, 559; V. Rodt, *Rec. trav. chim.*, 1930, **49**, 441; *A.*, 723; G. F. Hüttig and A. Zörner, *Z. Elektrochem.*, 1930, **36**, 259; *A.*, 723.

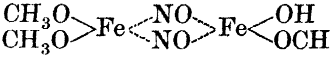
[29] J. B. Peel, P. L. Robinson, and C. L. Mavin, *Proc. Univ. Durham Phil. Soc.*, 1929, **8**, 153; *A.*, 179.

[30] F. de Rudder, *Bull. Soc. chim.*, 1930, [iv], **47**, 1225.

[31] W. Hieber, *Naturwiss.*, 1930, **18**, 33; A., 309; W. Hieber, F. Sonnenkalb, and E. Becker, *Ber.*, 1930, **63**, [*B*], 973; *A.*, 723.

[32] W. Hieber, K. Ries, and G. Bader, *Z. anorg. Chem.*, 1930, **190**, 193, 215; *A.*, 875.

[33] W. Hieber and E. Becker, *Ber.*, 1930, **63**, [*B*], 1405; *A.*, 1008.

It is said that the compound supposed by W. Manchot and H. Gall[34] to be Fe(NO),2MeOH is, in reality, a derivative of bivalent iron, with the structure  $\begin{smallmatrix}CH_3O\\CH_3O\end{smallmatrix}\!>\!Fe\!<\!\begin{smallmatrix}NO\\NO\end{smallmatrix}\!>\!Fe\!<\!\begin{smallmatrix}OH\\OCH_3\end{smallmatrix}$. By the action of nitric oxide on nickel carbonyl, a somewhat similar compound, $Ni(NO)(OCH_3)OH + CH_3OH$, was obtained.[35]

R. Brunner has described the preparation of several compounds from sodium nitroprusside,[36] and numerous compounds of hexamethylenetetramine with ferro- and ferri-cyanides have been obtained.[37]

A phase-rule study of the cobalt chloride colour change has been made, and the red salt $[Co(H_2O)_4]HgCl_4$ and the blue salt $[Mg\{(H_2O)_2\}_4]CoCl_4$ were isolated as well as several series of red solid solutions containing zinc chloride. Neither the simple dehydration theory nor the " variable co-ordination " theory of the colour changes is supported by the data. It is considered to be largely accidental that red cobalt chloride solutions contain red kations and blue solutions blue anions. In a more general way, the colour of cobaltous compounds is determined by the character of the electronic shift which is possible in the cobalt atom of the compound in question.[38] The electro-deposition of cobalt from red and from blue solutions has been examined, and found to be reversible only from the latter.[39]

The dehydration curves of hydrated cobaltous oxide prepared in different ways have been determined, as well as the catalytic activity of the metal reduced from various types of oxide.[40] The molybdates of various cobaltic ammines have been prepared.[41]

Vapour pressures of nickel carbonyl have been measured over the temperature range −35° to 40°.[42] Nickel thiosulphate forms a hexammine, a tetrammine, and a diammine, but not the pentammine described by Ephraim.[43] The dehydration curves and *X*-ray diagrams of hydrated nickelous and nickelic oxides have been examined.[44] The latter forms a monohydrate which breaks up irreversibly thus, $2(Ni_2O_3,H_2O) \longrightarrow 4NiO + 2H_2O + O_2$. According-ing to D. K. Goralevitsch,[45] colourless alkaline-earth salts of nickelic acid, H_2NiO_4, can be obtained by fusion of nickel oxide with potassium nitrate or chlorate and potassium hydroxide, followed by extraction with water and addition of the appropriate reagent to the green solution. $BaNiO_5$, NiO_4, and Ni_2O_5 are also said to have been obtained.[45a]

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[34] *Ann. Reports*, 1929, **26**, 66.

[35] H. Reihlen, A. Gruhl, G. von Hessling, and O. Pfrengle, *Annalen*, 1930, **482**, 161; *A.*, 1539.

[36] *Z. anorg. Chem.*, 1930, **190**, 384; *A.*, 1009.

[37] G. A. Barbieri, *Gazzetta*, 1930, **60**, 229; *A.*, 752.

[38] H. Bassett and H. H. Croucher, *J.*, 1930, 1784; *A.*, 1251.

[39] R. Brdička, *J. Czech. Chem. Comm.*, 1930, **2**, 489; *A.*, 1254.

[40] G. F. Hüttig and R. Kassler, *Z. anorg. Chem.*, 1930, **187**, 16, 24; *A.*, 543.

[41] P. R. Rây and S. N. Maulik, *J. Indian Chem. Soc.*, 1930, **7**, 607; *A.*, 1390.

[42] J. S. Anderson, *J.*, 1930, 1653; *A.*, 1104.

[43] L. le Boucher, *Anal. Fis. Quim.*, 1930, **28**, 895; *A.*, 1391.

[44] G. F. Hüttig and A. Peter, *Z. anorg. Chem.*, 1930, **189**, 183, 190; *A.*, 700.

The acetates of ruthenium have been described,[46] as well as some alkali-metal bromides of rhodium [47] and some rhodium pyridine bromides.[48] The ruthenium analogue of potassium nitroprusside, $K_2[Ru(CN)_5NO],2H_2O$ (also anhydrous), has been prepared by W. Manchot and J. Düsing;[48a] and by the action of carbon monoxide on ruthenium tribromide the compound RuBr(CO) containing univalent ruthenium has been obtained.[49]

The remarkable case of lithium platinocyanide, the trihydrate of which was supposed to become unstable with reference to the dihydrate at lower temperatures,[50] has been shown to have an entirely different explanation.[51]

By the action of sodium amalgam on solutions of potassium (or barium) platinocyanide or potassium palladocyanide, colourless, strongly reducing solutions are obtained which contain univalent platinum or palladium.[52]

The thermal decomposition of platinous and platinic sulphides has been studied, but no indication of any other sulphide was obtained.[53] Platinum diarsenide identical with the mineral sperrylite has been prepared.[54]

The brownish-yellow double salt $PtCl_2,2NH_3,4(PtCl_2,4NH_3)$ can form solid solutions in $PtCl_2,4NH_3,nH_2O$, and this is the cause of the yellowish-brown colour which the latter compound has when prepared by the action of ammonia on K_2PtCl_4.[55]

Numerous nitro-ammines of platinum have been described.[56]

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[45] *J. Russ. Phys. Chem. Soc.*, 1930, **62**, 897; *A.*, 1141.

[45a] *Idem, ibid.*, p. 1165; *A.*, 1540.

[46] A. W. Mond, *J.*, 1930, 1247; *A.*, 891.

[47] P. Poulenc, *Compt. rend.*, 1930, **190**, 639; *A.*, 559.

[48] *Idem, ibid.*, **191**, 54; *A.*, 1391. [48a] *Ber.*, 1930, **63**, [*B*], 1226.

[49] W. Manchot and E. Enk, *ibid.*, p. 1635; *A.*, 1141.

[50] J. E. Reynolds, *Proc. Roy. Soc.*, 1909, [*A*], **82**, 380; *A.*, 1909, i, 559.

[51] H. Terrey, *ibid.*, 1930, [*A*], **128**, 359; *A.*, 1141.

[52] W. Manchot and G. Lehmann, *Ber.*, 1930, **63**, [*B*], 2775; *A.*, 1931, 53; W. Manchot and H. Schmid, *ibid.*, p. 2782; *A.*, 1931, 53.

[53] W. Biltz and R. Juza, *Z. anorg. Chem.*, 1930, **190**, 161; *A.*, 861.

[54] L. Wöhler, *ibid.*, **186**, 324; *A.*, 440.

[55] N. S. Kurnakov and I. A. Andréevski, *Z. anorg. Chem.*, 1930, **189**, 137; *A.*, 560; *Ann. Inst. Platine*, 1929, **7**, 161; *A.*, 1930, 180.

[56] I. I. Tschernaiev, *ibid.*, 1929, **7**, 52; *A.*, 179; I. I. Tschernaiev and A. N. Fedorova, *ibid.*, p. 73; *A.*, 180; I. I. Tschernaiev and F. M. Klatschkin, *ibid.*, p. 84; *A.*, 180.

A large number of platinum tetrammine salts have been prepared and examined, and from the character of their electrical conductivity and absorption spectra it is concluded that they possess six co-ordinatively bound groups, and not four as hitherto assumed.[57] They should be formulated as $[Pt(NH_3)_4X_2]$, although in solvents such as water, alcohol, or acetone they are readily converted into stable salts of the type $[Pt(NH_3)_4(solvent)_2]\ X_2$.

The ammine amides of 4-valent platinum, such as

$$[Pt(NH_3)_4{\cdot}(NH_2){\cdot}Cl]Cl_2,$$

have been investigated with respect to their behaviour towards acids and bases.[58] Of the ammonia compounds examined, the 3-amido-diammine was the most basic. The behaviour of all the compounds is adequately represented by the equation $[R - Pt\ .\ .\ .\ NH_3]^{n+1} \leftarrow [R - Pt - NH_2]^n + H^{\cdot}$. Some interesting stereochemical questions are raised in two papers on platinum compounds by F. G. Angell, H. D. K. Drew, and W. Wardlaw,[59] and by F. G. Mann [60] respectively. These are dealt with in another section of the present volume (pp. 164, 166).

Systems and Equilibria.

Platinum–iron;[61] platinum–iridium;[62] rhodium–bismuth;[63] palladium–antimony;[64] gold–antimony;[65] iron–beryllium and iron–boron;[66] iron–manganese;[67] nickel–copper;[68] silver–copper;[69] cuprous iodide–silver iodide;[70] potassium selenate–water;[71] copper–oxygen;[72] titanium–hydrogen;[73] nitrogen pentoxide–nitric acid;[74] zirconium dioxide–beryllium oxide;[75] tellurium dioxide–hydrogen fluoride–water;[76] nickel–bismuth;[77] lead-germanium ;[78] silver–copper–zinc;[79] copper–tin–antimony;[80] potassium chlorate–sodium chlorate;[81] calcium chloride–cobalt (or iron, manganese, or cadmium) chloride;[81a] metal halides–hydrogen; metal halides–hydrogen chloride;[82] magnesium sulphate–sodium sulphate–water;[83] magnesium sulphate–sodium nitrate–water;[84] ammonium nitrate–potassium sulphate–water;[85] alumina–cryolite–chiolite;[86] acetic acid–acetate of potassium (or NH_4, Li, Pb, Ba, Ca, Zn); [87] iron–nitrogen;[88] nickel–chromium;[89] water–ether–uranyl nitrate or zinc iodide or cadmium iodide;[90] silver–aluminium–zinc;[91] sodium iodate–sodium sulphate–water;[92] sodium chloride–magnesium sulphate–water;[93] nickel–chromium;[94] ferrous sulphate–water;[95] calcium–calcium nitride; [96] iron–carbon–oxygen; [97] sodium hydroxide–sodium nitrate–water;[98] copper sulphate–sulphuric acid–water;[99] zinc oxide–zinc chloride–water;[1] potassium sulphate–

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magnesium sulphate–water;[2] water–alkali sulphate–sulphate of vitriol type;[3] magnesium sulphate–potassium nitrate–water;[4] magnesium chloride–sodium nitrate–water;[5] sodium dichromate–ammonium chloride–water;[6] potassium sulphate (or sulphuric acid)–hexamminocobaltic sulphate–water;[7] sodium palmitate–water–sodium chloride;[8] sodium germanate–sodium silicate and potassium germanate–germania;[8a] lead–antimony–magnesium;[9] potassium and calcium carbonates and hydroxides–water;[10] iron–manganese;[11] iron–silicon;[12] iron–nitrogen;[13] sodium sulphate–sodium carbonate–water;[14] sodium chloride–magnesium sulphate–water;[15] aluminium silicon–copper;[16] sodium (or potassium) bromide (or iodide)–water;[17] phenol–silver nitrate–water;[18] iron–nitrogen;[19] sodium oxide–silica;[20] sodium oxide–boric oxide–water;[21] sodium oxide–silica–zirconium dioxide;[22] calcium chlorate–potassium chloride–water;[23]

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[6] I. Gerasimov, *ibid.*, **187**, 321; *A.*, 702.

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iron–nickel–sulphur;[24] nickel–chromium;[25] $Ca + 2NaCl \rightleftharpoons 2Na + CaCl_2$;[26] carbamide–ammonium nitrate–sodium nitrate;[27] ammonium carbamate–carbamide–water–ammonia;[28] boric oxide–cæsium oxide–water;[29] lithium–silver;[30] cadmium–zinc;[31] lead–antimony;[32] lead–tin;[33] manganese oxide–cadmium oxide;[34] manganese oxide–magnesium oxide;[35] alumina–chromium sesquioxide;[35] alumina–ferric oxide;[35] chromium sesquioxide–ferric oxide;[35] iron–boron;[36] ammonium nitrate–water;[37] carbon dioxide–ammonia–water;[38] alumina–sodium (or potassium) oxide–water;[39] cadmium sulphate–potassium (or ammonium) sulphate–water;[40] potassium oxide–lime–silica;[41] $Fe + NiSiO_3 \rightleftharpoons Ni + FeSiO_3$;[42] silver–strontium and silver-barium;[43] water–hydrogen fluoride;[44] $K_2CO_3 + 2NaHCO_3 \rightleftharpoons Na_2CO_3 + 2KHCO_3$;[45] potassium carbonate, bicarbonate, and water;[46] sodium sulphate, fluoride, and chloride and water;[47] mercuric oxide–sulphur trioxide–water;[48] copper sulphate–

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lithium sulphate–water;[49] sodium chloride–magnesium sulphate–water (and related systems);[50] silver iodide–metal chlorides of Group I.[51]

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ORGANIC CHEMISTRY.

PART I.—ALIPHATIC DIVISION.

Pyrolysis of Hydrocarbons.

STUDY of the action of heat on paraffin hydrocarbons [1] has demonstrated that two types of reaction occur, degradative and additive. In the thermal decomposition of the normal paraffins rupture of the chain appears to occur at any position [2] with production of an olefin and the complementary lower paraffin or, at the limit, hydrogen. Methane represents a special case, possessing a higher decomposition point than its homologues. With this hydrocarbon little decomposition occurs below 1000°, at which temperature both ethylene and acetylene are formed; at higher temperatures under atmospheric pressure decomposition into carbon and hydrogen is practically complete. For the maximum production of ethylene and acetylene, reduced pressure is essential and at 1200°/100 mm., with suitable rates of flow, 4% of ethylene and 2·5% of acetylene are formed; above this temperature the quantity of ethylene diminishes to zero while the amount of acetylene increases (14·5% at 1500°/50 mm.). With *iso*butane, fission at CH linkings to yield hydrogen and *iso*butylene becomes a major reaction.

The formation of ethylene and acetylene from methane affords a simple instance of the additive reactivity which is concerned in the addition of olefin to olefin. To the interaction of the olefins which are produced at an early stage of the thermal decomposition of the paraffins, the formation of aromatic hydrocarbons is attributed. Consequently the behaviour of the olefins under the action of heat is a matter of considerable practical importance.

Examination of the thermal decomposition of ethylene, propylene, and the two *n*-butylenes [3] suggests that the principal primary reactions in each instance are the formation of either two-carbon or four-carbon olefins (or of both): $2C_2H_4 \longrightarrow C_4H_8$; $2C_3H_6 \longrightarrow$

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[1] For a review of the extensive literature dealing with the decomposition of paraffin hydrocarbons by thermal means, with and without catalysts, by electrical means, by photosensitisation, and by α-particles, see G. Egloff, R. E. Schaad, and C. D. Lowry, jun., *J. Physical Chem.*, 1930, **34**, 1617; *A.*, 1268.

[2] E. N. Hague and R. V. Wheeler, *J.*, 1929, 378; *A.*, 1929, 536; F. de Rudder and H. Biedermann, *Bull. Soc. chim.*, 1930, [iv], **47**, 704; *A.*, 1268; C. D. Hurd and L. U. Spence, *J. Amer. Chem. Soc.*, 1929, **51**, 3353, 3561; *A.*, 1930, 58, 191.

[3] R. V. Wheeler and W. L. Wood, *J.*, 1930, 1819; *A.*, 1399.

$C_2H_4 + C_4H_8$; $C_4H_8 \longrightarrow 2C_2H_4$. Thus polymerisation and degradation occur side by side, but the primary processes are speedily followed by dehydrogenation (a primary mode of decomposition in the case of butylene). In the presence of the hydrogen so liberated, the olefins decompose through the scission of the carbon chain at the last C—C linking, forming radicals which by hydrogenation produce methane and the next lower olefin: $CH_3{\cdot}CH{:}CH_2 \longrightarrow CH_3{\cdot} + {\cdot}CH{:}CH_2 \xrightarrow{H\cdot H} CH_4 + CH_2{:}CH_2$; $CH_3{\cdot}CH_2{\cdot}CH{:}CH_2 \longrightarrow CH_3{\cdot} + {\cdot}CH_2{\cdot}CH{:}CH_2 \xrightarrow{H\cdot H} CH_4 + CH_3{\cdot}CH{:}CH_2$. Butadiene, formed by dehydrogenation of butylene, is thought always to be present in the early stages of decomposition and it is suggested that the combination of ethylene and butylene, of propylene and butadiene, and of butylene and butadiene yields hydroaromatic hydrocarbons which at higher temperatures lose hydrogen to yield benzene and its homologues.

The degradation of the paraffins can be viewed as proceeding by the reversible elimination of a molecule HX, which may be either a paraffin of smaller molecular weight or hydrogen itself. The residue is then an olefin, and the process is comparable with the elimination of acid and water from any olefin addition product.[4]

The additive process can probably proceed in two ways, which are characteristic of olefin polymerisation and butadiene–olefin addition respectively. Both of these processes are discussed later (pp. 91, 88) and need no further mention here, but it would seem from recent developments in these directions that of the two mechanisms which have been suggested for the production of hydroaromatic compounds, *viz.* (1) direct butadiene–olefin addition and (2) the intermediate formation of (open-chain) hexadienes or hexatrienes by addition of olefin to olefin, the former is the more probable.

Carbon Unsaturation.

Mono-olefinic and Mono-acetylenic Compounds.—Inability to obtain homogeneous specimens or to determine the composition of mixtures of isomerides is frequently a great disadvantage of the common methods of olefin preparation. For this reason the discovery of a general method for obtaining pure Δ^{α}-olefins [5] by the action of zinc on β-alkyloxy-*n*-alkyl bromides, and the elaboration of a method for estimating the proportion of admixed Δ^{α}- and Δ^{β}-butenes [6] by determining the rate of reaction of their dibromides with potassium iodide, are of importance.

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[4] T. M. Lowry, *J.*, 1929, 378; *A.*, 1929, 536.

[5] H. B. Dykstra, J. F. Lewis, and C. E. Boord, *J. Amer. Chem. Soc.*, 1930, **52**, 3396; *A.*, 1269.

[6] R. T. Dillon, W. G. Young, and H. J. Lucas, *ibid.*, p. 1953; *A.*, 888; W. G. Young and H. J. Lucas, *ibid.*, p. 1964; *A.*, 888.

Announcements have been made with regard to the occurrence of an unexpected variety of isomerism in Δ^{β}-pentene.[7] The hydrocarbon as prepared by dehydrobromination of γ-bromopentane, or dehydration of diethylcarbinol, is reported to pass under the influence of ultra-violet light into an isomeride. This differs from the first compound only slightly in physical properties but very markedly with regard to the proportion of β- and γ-bromopentane produced therefrom by the action of hydrogen bromide. To explain the relationship of the isomerides, the absorption spectra of which differ sufficiently markedly to exclude their representation as *cis*- and *trans*-isomerides, a species of electronic isomerism dependent on unequal sharing of electrons at the double linking is postulated.

The observation that *cis*-forms of ethylene compounds suffer catalytic reduction more readily and smoothly than the *trans*-varieties has been found to apply to *iso*crotonic acid, to *iso*stilbene, and to *cis*-*o*-hydroxy- and *cis*-*o*-ethoxy-cinnamic acids, all of which are more readily reduced to saturated acids than are the corresponding *trans*-compounds.[8] On applying the method to confirm the configurations of erucic and brassidic acid, it is found that the difference in their rate of hydrogenation (to behenic acid) is less marked than in the case of oleic and elaidic acids, but is sufficient to establish them as the *cis*- and *trans*-forms of the acid

$$CH_3\cdot[CH_2]_7\cdot CH\colon CH\cdot[CH_2]_{11}\cdot CO_2H.$$

In spite of contradictory results obtained by other methods it appears from the study of eleven triple-bonded substances of different types that hydrogenation of acetylenes in the presence of colloidal palladium stabilised by starch uniformly gives the *cis*-ethylenic derivative.[9]

The very different courses followed by hydrogenation processes have caused considerable speculation as to the state of hydrogen (H^+, $H^{(n)}$, or H^-) entering into reaction. By employment of an apparatus recently described, the action on organic compounds of atomic hydrogen from a Geissler tube may be ascertained.[10] Oleic acid and ethyl phthalate are reduced thereby, but considerable quantities of polymeric materials are produced in each instance.

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[7] M. S. Kharasch and F. R. Darkis, *Chem. Reviews*, 1928, **5**, 571; E. P. Carr, *J. Amer. Chem. Soc.*, 1929, **51**, 3041; *A.*, 1929, 1420; M. L. Sherrill, C. Baldwin, and D. Haas, *ibid.*, p. 3034; *A.*, 1929, 1419.

[8] C. Paal and H. Schiedewitz, *Ber.*, 1930, **63**, [*B*], 766; *A.*, 740.

[9] M. Bourguel, *Bull. Soc. chim.*, 1929, [iv], **45**, 1067; *A.*, 1930, 317. Compare J. S. Salkind and V. K. Teterin, *J. Russ. Phys. Chem. Soc.*, 1929, **61**, 1751; *A.*, 1930, 574.

[10] W. Nagel and E. Tiedemann, *Wiss. Veröff. Siemens-Konz.*, 1929, **8**, [2], 187; *A.*, 1930, 577.

The action of sulphur[11] and of amines[12] in bringing about *cis-trans* transformation of ethylenic acids has been studied. The conversion of methyl maleate into methyl fumarate is catalysed by ammonia and primary or secondary amines, but not by tertiary amines. Mechanisms are suggested for this transformation and for the Knoevenagel reaction: in the one case the disappearance of the configurational constraint associated with the double bond and in the other the production of appropriate kationic and anionic forms of the reactants are considered to be the consequence of the formation of co-ordinate links between the hydrogen atom of the base and carbonyl oxygen $>\overset{\curvearrowright}{C{=}O} \longrightarrow HX$. For the former reactivity, however, the suggested mechanism is improbably of general applicability, since there is reason to believe that in some instances the *cis-trans* isomerisation of Knoevenagel products (although not the formation) involves $\alpha\beta,\beta\gamma$-isomerisation[13] and with regard to the latter there is as yet no conclusive evidence to show that the Knoevenagel reaction is uniquely a reaction involving the non-enolised carbonyl group of a ketone or aldehyde, although there is much evidence to show that the reaction is not dependent on the enolisation of the carbonyl group.[14]

The question of catalytic mechanism arises again in connexion with the Michael reaction. As the result of the work of J. F. Thorpe[15] on the addition of ethyl sodio-α-cyanopropionate to ethyl ββ-dimethylacrylate the conclusion was unavoidable that in this instance *either* addition could occur to some extent by partition of the sodio-addendum in the manner $Me{-}\vdots{-}\overset{Na}{\overbrace{C(CN)\cdot CO_2Et}}$, *or*, if addition did indeed involve the partition $Na{-}\vdots{-}CMe(CN)\cdot CO_2Et$ in the way usually supposed to be characteristic of the Michael reaction, then the product could be further alkylated by methyl iodide at the α-carbon atom of the resulting sodio-ββγ-trimethyl-γ-cyanoglutaric ester, $EtO_2C\cdot CMe(CN)\cdot CMe_2\cdot\overset{Na}{\overbrace{CH\cdot CO_2Et}}$. Thorpe held the view that the methyl group in the methyl-cyano-ester and the hydrogen atom in the corresponding unmethylated cyano-ester actually separated, the sodium atom remaining in the ester residue.

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[11] G. Rankoff, *Ber.*, 1929, **62**, [*B*], 2712; 1930, **63**, [*B*], 2139; *A.*, 1930, 65, 1406.

[12] G. R. Clemo and S. B. Graham, *J.*, 1930, 213; *A.*, 452.

[13] E. H. Farmer and J. Ross, *J.*, 1926, 1570; *A.*, 1926, 834.

[14] J. C. Bardhan, *ibid.*, 1929, 2225; 1930, 1509; *A.*, 1929, 1462; 1930, 1170; C. K. Ingold, *ibid.*, p. 184; *A.*, 1170.

[15] *Ibid.*, 1900, **77**, 923. Compare A. Michael, *Ber.*, 1900, **33**, 3731; *A.*, 1901, i, 123.

Convincing evidence has been furnished to show that in the presence of a full molecular proportion of sodium ethoxide the partition of ethyl methylmalonate involves *entirely* the separation of the methyl group as kationic component; with a fractional molecular proportion (conveniently $\frac{1}{6}$), however, the methyl group for the most part remains attached to the ester residue, but to a minor extent (about 10%) separates as the kationic fragment.[16] The action of sodium ethoxide in small proportion is considered to be purely catalytic, contributing towards a reaction mechanism comparable with that encountered in catalytic *cis-trans*-ethenoid isomerisation, but differing from that which governs addition when the addendum is a sodium enolate.[17] Strong ground is afforded for presuming that the characteristic partition of non-alkylated sodio-addenda (sodium enolates) involves the separation of hydrogen and not of sodium.

Investigations relating to the manner of addition to olefins of hydrogen halides,[18] carbonyl chloride,[19] and halogenated amines [20] have been carried out. The results are of importance as reflecting broadly the polar influence of the ethylenic substituents on the competitive formation of alternative additive products ($>C_1X{\cdot}\check{C}_2Y$ and $>C_1Y{\cdot}\check{C}_2X$), but as yet the quantitative data available in this important field are few.

Polyolefinic and Polyacetylenic Compounds.—With the recognition that the substances reputed to be αα-dimethylbutadiene [21] and β-*cyclo*propylpropene [22] are actually αγ- and αα-dimethyl-butadiene respectively, the series of monomethyl- and dimethyl-butadienes becomes complete. It is now abundantly clear from the manner in which bromine becomes added to the αδ-, αγ-, and βγ-dimethylbutadienes [23] that the formation of both adjacent and terminal dibromides must be regarded as embodying *primary* reactivities of the conjugated molecule: that is to say, the formation of αδ-, αζ-, etc., additive compounds is not to be regarded as taking place *via* the formed molecules of corresponding αβ-compounds. It is equally apparent that the bromination products, one or all in each case, are not necessarily mobile. The new facts are consistent with the additive mechanism of H. Burton and C. K. Ingold,[24] but run counter (as in the writer's view do all the observations of the last few years concerning additive processes in relation to anionotropic change) to a more recent formulation.[25] The latter is compatible with the possession by a butadiene of two potential structures, di-ethylenic and conjugated, and obscures the strong experimental indication that the orientation of the additive products is related to the double degree of unsaturation only to the extent that the latter is able to contribute to the formation of a mobile propene system when once simple ethylenic addition has been initiated. In this connexion it is interesting to note that examination of the Raman spectra of butadiene, piperylene, isoprene, and βγ-dimethylbutadiene has shown no reason for assuming that the C:C linking in conjugated systems, whether open or closed, is in a state distinct from that of an ordinary double linking of the allyl type.[26]

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[16] A. Michael and J. Ross, *J. Amer. Chem. Soc.*, 1930, **52**, 4600.

[17] For non-catalytic addition the addendum in the case of ethyl malonate is represented by $H^{--}C(CO_2Et):C(ONa){\cdot}OEt$, analogous to J. F. Thorpe's representation of ethyl sodiocyanoacetate.

[18] C. C. Coffin, H. S. Sutherland, and O. Maass, *Canad. J. Res.*, 1930, **2**, 267; *A.*, 888; R. Lespieau, *Bull. Soc. chim.*, 1930, [iv], **47**, 847; *A.*, 1401

[19] E. Pace, *Gazzetta*, 1929, **59**, 578; *A.*, 1929, 1419.

[20] Z. Földi, *Ber.*, 1930, **63**, [*B*], 2257; *A.*, 1423.

[21] O. Diels and K. Alder, *Annalen*, 1929, **470**, 98; *A.*, 1929, 819; E. H. Farmer, C. D. Lawrence, and W. D. Scott, *J.*, 1930, 510; *A.*, 572.

[22] P. Bruylants, *Bull. Acad. roy. Belg.*, 1908, 1011; *A.*, 1909, i, 226; N. van Keersbilck, *Bull. Soc. chim. Belg.*, 1929, **38**, 205; *A.*, 1929, 1163.

[23] E. H. Farmer, C. D. Lawrence, and W. D. Scott, *loc. cit.*

The variable addition to conjugated substances demonstrated for halogen addition has now been shown to characterise sodio-ester addition [27] and hydrogenation (non-catalytic).[28] Esters of the malonic type yield both αβ- and αδ-addition products with the esters of the butadiene-α-carboxylic acids and likewise the reduction of the latter acids by metals which react with water gives both Δ^{γ}- and Δ^{β}-butenecarboxylic acids. In all these instances there appears to exist a definite ratio between the amounts of the αβ- and αδ-products formed which depends largely on the constitution of the conjugated compound but to some extent on other factors. For example, methyl substitution at the δ-, β-, and βδ-carbon atoms in β-vinylacrylic acid causes a change in the proportion of the αβ- and αδ-reduction products in the direction required by considerations of prototropy, with which hydrogen addition has been correlated.[24] It must be remembered, however, that the experimental methods available for estimating the αβ,αδ ratio in all additive processes leave much to be desired and at present the significance of quantitative results is not to be rated too highly.

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[24] *J.*, 1928, 912; *A.*, 1928, 634. Some misconception has arisen (compare I. E. Muskat and H. E. Northrup, *J. Amer. Chem. Soc.*, 1930, **52**, 4048; *A.*, 1553) from a statement of these authors to the effect that in the addition of halogens the initial product could only be a 1 : 2-compound. It seems clear from the context and from a subsequent re-statement (*Ann. Reports*, 1928, **25**, 132) that the authors have in mind the attack by the reagent at a single ethylenic centre and not the actual formation of the αβ-dibromide.

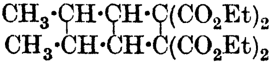
[25] *Ann. Reports*, 1929, **26**, 121.

[26] A. Dadieu and K. W. F. Kohlrausch, *Ber.*, 1930, **63**, [*B*], 1657; *A.*, 1162.

[27] E. H. Farmer and T. N. Mehta, *J.*, 1930, 1610; *A.*, 1163.

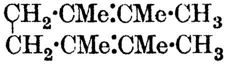
[28] J. T. Evans and E. H. Farmer, *Chem. and Ind.*, 1928, **47**, 268; *J.*, 1928, 1644; *A.*, 1928, 868.

In many reductions of butadiene acids by metals simple reduction products are not solely or principally formed, but in their place hydrogenated double molecules appear.[29] These are (so far as has been ascertained) linked at the β-carbon atoms and are prone to undergo secondary intramolecular change as illustrated by the formation of a *bicyclo*hexane derivative (A, below) from ethyl crotylidenemalonate. A similar type of reductive polymerisation is that whereby isoprene passes on treatment with potassium and alcohol to a mixture of βζ-, βη-, and γζ-dimethyl-$\Delta^{\beta\zeta}$-octadiene whilst βγ-dimethylbutadiene passes with the same reagents to a mixture of βγζη-tetramethyl-$\Delta^{\beta\zeta}$-octadiene (B) and methyl rubber[30]; the interesting observation is also made that isoprene may be simultaneously ethylated and reduced by the action of potassium and ethyl bromide to yield δ-methyl-Δ^{δ}-octene.



$$\begin{array}{llll}\mathrm{CH_3\cdot} & \mathrm{CH} & \mathrm{\cdot CH} & \mathrm{\cdot C(CO_2Et)_2}\\ & | & | & |\\ \mathrm{CH_3\cdot} & \mathrm{CH} & \mathrm{\cdot CH} & \mathrm{\cdot C(CO_2Et)_2}\end{array}$$

(A.)



$$\begin{array}{ll}\mathrm{CH_2} & \mathrm{\cdot CMe{:}CMe\cdot CH_3}\\ | & \\ \mathrm{CH_2} & \mathrm{\cdot CMe{:}CMe\cdot CH_3}\end{array}$$

(B.)

The simple addition products of the butadienes are for the most part oily substances and no satisfactory means of characterising the hydrocarbons has been available. Owing to the discovery that maleic anhydride, acetaldehyde, acraldehyde, acrylic ester, *p*-benzoquinone, α-naphthaquinone, and other substances possessing the group CH:CH·CO unite quantitatively with the butadienes, frequently when the reactants are mixed at room temperature,[31] an elegant and trustworthy method of characterisation is provided. In addition, the underlying reaction is of great synthetic value and presents a number of points of theoretical and practical interest which may be summarised thus : (1) No single instance has been discovered in which other than complete terminal attachment of the non-dividing addendum occurs, so that all the known products may be typified by those derived from the combinations isoprene–maleic anhydride, butadiene–acraldehyde, and butadiene–benzoquinone, (I), (II), and (III), respectively.

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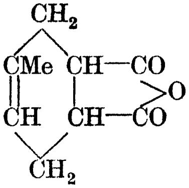
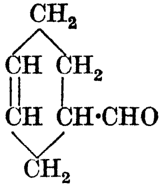
[29] C. M. Cawley, J. T. Evans, and E. H. Farmer, *J.*, 1930, 522; *A.*, 578.

[30] T. Midgley, jun., and A. L. Henne, *J. Amer. Chem. Soc.*, 1929, **51**, 1293, 1294; 1930, **52**, 2075, 2077; *A.*, 1929, 674; 1930, 888.

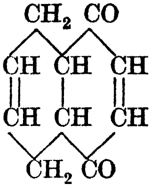
[31] O. Diels and K. Alder, *Annalen*, 1928, **460**, 98; *A.*, 1926, 1018; O. Diels, K. Alder, and E. Naujoks, *Ber.*, 1929, **62**, [*B*], 554; *A.*, 1929, 570; O. Diels, K. Alder, W. Lübbert, E. Naujoks, F. Querberitz, K. Röhl, and H. Segeberg, *Annalen*, 1929, **470**, 62; *A.*, 1929, 819; O. Diels, K. Alder, and P. Pries, *Ber.*, 1929, **62**, [*B*], 2081; *A.*, 1929, 1297.



(I.)



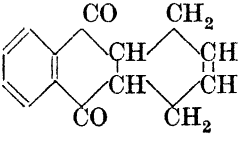
(II.)



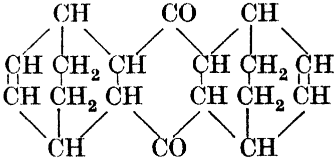
(III.)

(2) The butadiene acids (*e.g.*, sorbic and muconic acids) yield carboxylated tetrahydrophthalic anhydrides with maleic anhydride,[32] but in the formation of these, $\beta\gamma,\alpha\beta$-double bond change may occur.

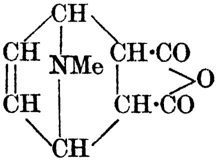
(3) Cyclic butadienoid compounds (*cyclo*pentadiene, *cyclo*hexa diene, furan, *N*-methylpyrrole) yield bridged anhydro*cyclo*hexenes on treatment with maleic anhydride; [31] benzoquinone may unite with one or with two molecular equivalents of open-chain or cyclic butadienes to yield hydronaphthaquinone and hydroanthraquinone derivatives respectively; [33] α-naphthaquinone combines with one molecular equivalent of open-chain or cyclic butadiene to yield hydroanthraquinone derivatives. The compounds arising from the combinations butadiene–α-naphthaquinone, *cyclo*hexadiene (2 mols.)–benzoquinone (1 mol.), *N*-methylpyrrole–maleic anhydride are represented by (IV), (V), and (VI).



(IV.)



(V.)



(VI.)

Many of the hydroanthraquinone derivatives, including (V), are convertible into the corresponding anthraquinones.

(4) The hexatrienes and higher poly-ene hydrocarbons also yield *cyclo*hexene derivatives; *e.g.*, both the *cis*- and the *trans*-form of hexatriene yield the same ethylidene*cyclo*hexene [32] (VII) with maleic anhydride, whilst αθ-diphenyloctatetraene unites with the same reagent (even one molecular equivalent only) straightway to give (VIII).[34] The course of reaction of the higher hydrocarbons of structure $Ph{\cdot}[CH{:}CH]_n{\cdot}Ph$ appears to be dominated by the strong reactivity of the terminal methine groups, so that with ακ-diphenyl-

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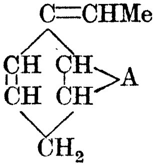
[32] E. H. Farmer and F. L. Warren, *J.*, 1929, 897; *A.*, 1929, 812.

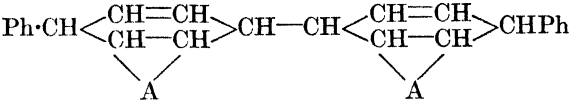
[33] O. Diels, K. Alder, G. Stein, P. Pries, and H. Winckler, *Ber.*, 1929, **62**, [*B*], 2337; *A.*, 1929, 1303.

[34] R. Kuhn and T. Wagner-Jauregg, *Ber.*, 1930, **63**, [*B*], 2662; *A.*, 1580.

decapentaene, and apparently with still higher members of the series, *cyclo*hexene formation is initiated at both ends of the unsaturated chain as would be anticipated.



(VII.)



[A = ·CO·O·CO·]

(VIII.)

When many of the pairs of reactants in the Diels–Alder reaction are mixed, colorations rapidly appear, which disappear when reaction is complete. These probably mark the first stage of addition,[32, 34] presumably corresponding to attachment of the addendum at one end of the conjugated system. Another interesting observation concerns the colour of conjugated hydrocarbons themselves.[35] It has been concluded from the study of synthetic and natural dyes that an aliphatic hydrocarbon must possess 5—6 double bonds in unbroken conjugation for colour to develop; moreover, the colour-conferring value of a free carboxyl group conjugated with double linkages would seem to correspond to about $1\frac{1}{2}$ double linkages. On this basis the first member of the sorbic acid series which would be expected to show absorption bands extending into the visible part of the spectrum is decatetraenoic acid, $CH_3\cdot[CH{:}CH]_4\cdot CO_2H$. By the isolation of both octatetraenoic acid and decatetraenoic acid this expectation has been fulfilled, since the former acid is colourless whilst the latter is intensely yellow.

The constitution of the well-known crystalline compound of isoprene and sulphur dioxide has now been elucidated.[36] The sulphur dioxide acts as a non-dividing addendum and in this instance becomes attached at the terminal carbon atoms of the isoprene chain, yielding β-methyl-Δ^{β}-butene-αδ-sulphone.

By the action of iodine (2 atoms) on acetylenic Grignard reagents of the type CR⋮CMgX (2 mols.) a series of conjugated diacetylenes (R·C⋮C·C⋮CR) has been obtained.[37] These include $\Delta^{\delta\zeta}$-decadi-inene, $\Delta^{\epsilon\eta}$-dodecadi-inene, $\Delta^{\zeta\theta}$-tetradecadi-inene and αδ-diphenyldiacetylene. The behaviour of the last of these when catalytically hydrogenated is remarkable : the product contains both dihydro-

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[35] R. Kuhn and M. Hoffer, *Ber.*, 1930, **63**, [*B*], 2164; *A.*, 1406.

[36] E. Eigenberger, *J. pr. Chem.*, 1930, [ii], **127**, 307; *A.*, 1405.

[37] V. Grignard and Tchéoufaki, *Compt. rend.*, 1929, **188**, 357, 1531; *A.*, 1929, 290, 907.

and tetrahydro-derivatives which in form at least are representable as products of αδ-, αβγδ-, and ααδδ-addition.

$$\mathrm{CPh\vdots C{\cdot}C\vdots CPh} \longrightarrow \left\{\begin{array}{l}\mathrm{CHPh{:}C{:}C{:}CHPh} \\ \mathrm{CHPh{:}CH{\cdot}CH{:}CHPh}\ (\textit{cis-cis}) \\ \mathrm{CH_2Ph{\cdot}C\vdots C{\cdot}CH_2Ph}\end{array}\right.$$

Polymerisation.

Hydrocarbons.—The more immediate problems connected with the formulation of the additive and degradative processes associated with the different stages of polymerisation and depolymerisation of olefinic hydrocarbons concern (1) the structure of dimerides and the uniformity (or otherwise) of the additive processes underlying their formation, and (2) the genetic relationship of monomerides and higher polymerides.

as-Diphenylethylene gives an unsaturated dimeride, ααγγ-tetraphenyl-Δ^{β}-butene, by the action of aluminium chloride, iodine, or sulphuric acid. The last reagent, however, converts the unsaturated dimeride initially produced into a saturated isomeride which (like the dimeride obtained by the action of aluminium chloride on stilbene) has been deemed to be a derivative of *cyclo*butane.[38] It is now shown that the saturated dimeride is 1 : 3 : 3-triphenylhydrindene, formed by a simple cyclisation of the unsaturated isomeride.[39] Likewise a specimen of di*iso*butylene has been shown to contain βδδ-trimethyl-Δ^{β}- and -Δ^{α}-pentenes.[40]

The formation of *cyclo*butane derivatives cannot be considered as a characteristic of the dimerisation of mono-olefins : indeed such polymerisation is increasingly found to conform to an additive type which resembles the Michael reaction in that hydrogen separates from the addendum molecule, the components becoming added at the double bond of the second molecule :

$$\mathrm{CPh_2{:}CH[H] + CPh_2{:}CH_2 \longrightarrow CPh_2{:}CH{\cdot}CPh_2{\cdot}CH_3}$$

Addition of precisely this kind appears to account for the syntheses of open-chain olefins during the pyrolysis of hydrocarbons (p. 82) and for the production of Δ^{α}-butene and Δ^{α}-hexene from ethylene under the action of an electric discharge.[41] The latter result is particularly noteworthy, since not only is 80—90% of the ethylene converted into the butene–hexene mixture, but there is definite experimental indication that the polymerisation proceeds in the stages

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[38] S. V. Lebedev, I. A. Andreevski, and A. A. Matinschkina, *J. Russ. Phys. Chem. Soc.*, 1922, **54**, 223; *A.*, 1923, i, 770; H. Wieland and E. Dorrer, *Ber.*, 1930, **63**, [*B*], 404; *A.*, 464.

[39] E. Bergmann and H. Weiss, *Annalen*, 1930, **480**, 49, 59; *A.*, 901, 902; C. S. Schoepfle and J. D. Ryan, *J. Amer. Chem. Soc.*, 1930, **52**, 4021; *A.*, 1568.

[40] R. J. McCubbin and H. Adkins, *ibid.*, p. 2547; *A.*, 1017.

[41] G. Mignonac and R. V. de Saint-Aunay, *Compt. rend.*, 1929, **189**, 106; *A.*, 1929, 1037.

$$CH_2{:}CH_2 \xrightarrow{C_2H_4} CH_2{:}CH{\cdot}CH_2{\cdot}CH_3 \xrightarrow{C_2H_4} CH_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3.$$

The mechanism underlying the polymerisation brought about when acetylene is submitted to an electric discharge is not quite so clear, but, since a mixture of dipropargyl, γ-methyl-$\Delta^{\alpha\delta}$-pentadiinene, and diethenylacetylene is produced,[42] addition probably proceeds in an analogous way—first giving ethinylethylene, which unites with acetylene in more than one way. The process would seem to become somewhat modified when the polymerisation is effected by heat.[43] Acetylene begins to polymerise at about 300°, polymerisation continuing as the only reaction of importance up to 600°. To a large extent benzene and other aromatic hydrocarbons are produced. Analogously, methylacetylene might be expected to yield mesitylene and other aromatic hydrocarbons : instead, it first suffers three-carbon isomerisation into allene, ultimately yielding (as does allene when taken initially) a mixture of dimeride, trimeride, and higher polymerides, but apparently no aromatic hydrocarbons.

For the polymerisations brought about by the action of electric discharge [44] and ultra-violet light [45] on saturated paraffins, however, quite different mechanisms are suggested. These involve not degradation to olefins, succeeded by polymerisation, but polymerisation with hydrogen fission as indicated for the respective processes in (1) and (2) :

$$(1)\quad C_4H_{10} \longrightarrow C_4H_{10}{}^+ + E^-;\quad C_4H_{10} + C_4H_{10}{}^+ \longrightarrow (C_4H_{10}{\cdot}C_4H_{10})^+ \xrightarrow{E^-} C_8H_{18} + H_2.$$

$$(2)\quad nC_2H_6 \longrightarrow (n-1)H_2 + C_{2n}H_{4n+2}.$$

The products, however, are not wholly saturated.

The synthetic relationship of the monomeride, dimeride, trimeride, etc., of olefins such as *iso*butylene has long been a subject of interest but has not been satisfactorily determined. It has now been shown, however, that, whereas *iso*butylene when heated in a glass tube at

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[42] G. Mignonac and R. V. de Saint-Aunay, *Compt. rend.*, 1929, **188**, 959; *A.*, 1929, 537.

[43] R. N. Pease, *J. Amer. Chem. Soc.*, 1929, **51**, 3470; *A.*, 1930, 58; R. N. Meinert and C. D. Hurd, *ibid.*, 1930, **52**, 4540; *A.*, 1931, 61; P. Schläpfer and M. Brunner, *Helv. Chim. Acta*, 1930, **13**, 1125; *A.*, 1400.

[44] S. C. Lind and G. Glockler, *J. Amer. Chem. Soc.*, 1929, **51**, 3655; *A.*, 1930, 190.

[45] W. Kemula, *Rocz. Chem.*, 1930, **10**, 273; *A.*, 887.

200° yields only tri*iso*butylene, and when treated with sulphuric acid yields the trimeride with a very small amount of dimeride, yet if polymerised by contact with Florida earth it yields polymerides recognisably ranging from di- to hepta-merides along with higher polymerides which suffer depolymerisation on attempted distillation.[46] Although prolongation of the period of contact of hydrocarbon and earth leads to an increase in the proportion of the more highly polymerised forms, not all the individual polymerides seem to suffer further polymerisation. Indeed, the changes which take place appear to be the following :

$$C_4H_8 + C_4H_8 \longrightarrow (C_4H_8)_2;\ (C_4H_8)_2 + C_4H_8 \longrightarrow (C_4H_8)_3;$$
$$2(C_4H_8)_2 \longrightarrow (C_4H_8)_4;\ (C_4H_8)_2 + (C_4H_8)_3 \longrightarrow (C_4H_8)_5.$$

The polymerising action may be reversed by heating the products at 200° in contact with the catalyst.[47] By studying the decomposition of the individual polymerides it is found that each one of the foregoing polymerisations may be reversed but in all cases some monomeric *iso*butylene is produced, attributed in the cases of the tetra- and penta-merides to progressive dissociation of the initial di- and tri-meric forms. Practical difficulties have prevented a study of the decomposition of the higher polymerides, but it has been noted that prolonged contact of the polymeric forms with floridin at a high temperature causes the production of stable forms of high molecular weight. Di*iso*butylene is the most stable polymeric variety and the stability rapidly decreases with increasing molecular weight.

Halogeno-olefins.—Allyl chloride is converted in the absence of air, slowly on keeping, but more rapidly under the influence of ultra-violet light, into polyallyl chloride, $(C_3H_5Cl)_n$, which is not a single substance but a mixture of polymerides[48] (mean value of $n = 10$), formed by normal valency unions and probably possessing the structure :

$$\cdots\cdot CH_2\cdot CH(CH_2Cl)\cdot[CH_2\cdot CH(CH_2Cl)]_n\cdot CH_2\cdot CH(CH_2Cl)\cdot\cdots$$

The polymeride may be separated by fractional precipitation and extraction methods into a series of polymerides (n = 9, 12, 5, 25, 11, and 7) which decrease in solubility with increase in molecular weight.

Vinyl bromide and *as*-dichloroethylene also polymerise in the light to yield non-homogeneous substances, the components of which represent different stages of polymerisation.[49] Owing to inferior solubility in cold and instability (leading to dehydrobromination) in hot solvents the molecular weight cannot be determined. The polyvinyl bromide obtained from the former suffers replacement of the halogen atoms by methyl groups when treated with zinc methyl (ethyl groups with zinc ethyl) to yield a hydrocarbon $(C_5H_8)_x$ which resembles *cyclo*caoutchouc and is less unsaturated than caoutchouc; from indications afforded by reduction experiments it appears to consist of a mixture of long straight-chain compounds. The *as*-polydichloroethylene from the latter may be fractionated by extraction from benzene and reduced to hydrocarbons of widely differing molecular weight. It is completely saturated and to it is assigned the formula :

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[46] S. V. Lebedev and G. G. Kobliansky, *Ber.*, 1930, **63**, [*B*], 103; *A.*, 316.

[47] *Idem*, *ibid.*, p. 1432; *A.*, 1017.

[48] H. Staudinger and T. Fleitmann, *Annalen*, 1930, **480**, 92; *A.*, 889.

[49] H. Staudinger, M. Brunner, and W. Feist, *Helv. Chim. Acta*, 1930, **13**, 805; *A.*, 1402; H. Staudinger and W. Feist, *ibid.*, p. 832; *A.*, 1402.

$$\cdots\cdot CH_2{\cdot}CCl_2{\cdot}[CH_2{\cdot}CCl_2]_x{\cdot}CH_2{\cdot}CCl_2 \cdot\cdots \quad [x = 50\text{—}100].$$

Poly-esters.—The polymerism of the glycol esters of dibasic acids is a polymerism of intermolecular condensation and not of the addition of monomeric species. When in the interaction of $R(CO_2H)_2$ with $R'(OH)_2$ the number of atoms in the system $[{\cdot}CO{\cdot}R{\cdot}CO{\cdot}O{\cdot}R'\text{–}O{\cdot}]$ is too great to permit of five- or six-membered ring formation, the reaction becomes polymolecular and the polymerides are usually linear in type. The ethylene, trimethylene, hexamethylene, and decamethylene esters of malonic, adipic, and sebacic acids have been obtained [50] as crystalline compounds and all are highly polymerised: the structural unit ranges from 7 to 22 atoms and the molecular weight from 2300 (ethylene malonate) to 5000 (trimethylene sebacate). Ethylene and trimethylene carbonates are obtainable, as would be expected, in the monomeric form, but the latter can be converted on heating with potassium carbonate into a true polymeride, from which the monomeric ester is regenerated on distillation in a vacuum.

Neutral and acidic ethylene succinates showing different degrees of polymerisation have been prepared,[51] and mixed polymerides have been obtained by the interaction of ethylene glycol with equivalent quantities of succinic and sebacic acids, but not by fusing together (polymerised) ethylene succinate and ethylene sebacate. Both chemical and osmotic methods give concordant values for the molecular weights of these substances.

Monomeric ethylene oxalate is obtainable but gradually polymerises at room temperature and rapidly on heating. By extraction of a partly polymerised ester with acetonitrile, soluble and insoluble polymerides have been extracted, either of which can arise spontaneously from the other on keeping at the ordinary temperature.

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[50] W. H. Carothers and J. A. Arvin, *J. Amer. Chem. Soc.*, 1929, **51**, 2560; *A.*, 1929, 1165; W. H. Carothers and F. J. van Natta, *ibid.*, 1930, **52**, 314; *A.*, 319.

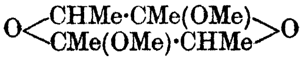
[51] W. H. Carothers and G. L. Dorough, *ibid.*, p. 711; *A.*, 452; W. H. Carothers, J. A. Arvin, and G. L. Dorough, *ibid.*, p. 3292; *A.*, 1272.

A similar process of polyintermolecular reaction occurs when ι-hydroxydecoic acid is heated alone or with various inert solvents.[52] Mixtures of acids of the type

$$HO\cdot[CH_2]_x\cdot CO_2\cdot([CH_2]_x\cdot CO_2\cdot)_n\cdot[CH_2]_x\cdot CO_2H$$

are produced, the components of which are partly separable by fractional crystallisation, and have molecular weights ranging from about 1000 to 9000. These complex acids yield the original acid on hydrolysis.

Dimeric Acetoins.—An important example which differs from all the polymeric types discussed above is that of acetoin.[53] Observations of the ultra-violet absorption spectrum of the monomeric form of this substance indicate the presence of the carbonyl group and hence of the preponderating, if not exclusive, existence of the keto-form, COMe·CHMe·OH. There are two crystalline dimerides of acetoin which give almost the same extinction curve in alcohol as the monomeride. It is clear that dissolution in alcohol does not cause fission of the dimerides, since they can be recovered crystalline after some hours, and molecular-weight determinations of the isomeride of higher melting point in the boiling solvent give normal values which decrease only when ebullition is prolonged. In the two crystalline forms it would seem, therefore, that the two acetoin molecules are united in such a manner that the keto-group, and consequently the whole acetoin molecule, remains unchanged in its main valency arrangement.

The possibility that groups other than carbonyl can give a similar extinction curve is negatived by observations with epichlorohydrin and triacetyl glucose anhydride. A dioxan structure is excluded, since dioxan itself is non-absorbent. Two ethereal oxygen atoms attached to the same carbon atom do not cause absorption, as is shown by the behaviour of methoxyacetaldehyde dimethylacetal. The dimeric methylacetal of acetoin does not exhibit the characteristic ketonic absorption, and hence is regarded as a dioxan derivative,  $O<\begin{matrix}CHMe\cdot CMe(OMe)\\CMe(OMe)\cdot CHMe\end{matrix}>O$, a view that is in harmony with its relatively difficult polymerisation. From the fact that the dimeric acetoins have considerably higher melting points when very rapidly heated than when very slowly heated it appears probable that the transformation temperature of the dimerides into the monomeride lies below the melting point.

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[52] W. H. Lycan and R. Adams, *J. Amer. Chem. Soc.*, 1929, **51**, 3450; *A.*, 1930, 65.

[53] W. Dirscherl and E. Braun, *Ber.*, 1930, **63**, [*B*], 416; *A.*, 454.

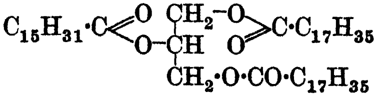
To account for the properties of dimeric acetoin a structure, $[\mathrm{Me{\cdot}\overset{|}{C}O{\cdot}CHMe{\cdot}\overset{|}{O}H}]_2$, has been proposed in which the association of molecules is dependent on the exercise of definitely located auxiliary valency forces. On account of the divergence of views as to the nature of the associative links holding in such highly polymerised substances as the polysaccharides, the further investigation of such relatively simple examples of residual valency polymerism as appear, from the evidence discussed, to be presented by the acetoins will be awaited with interest.

Alcohols and Ketones.

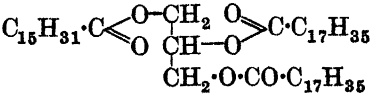
It was clearly desirable, for reasons discussed in last year's Report, that all supposed esterifications in the β-position of glycerol should be subjected to careful scrutiny. Further study of the constitution of a number of supposed β-monoglycerides [54] supports the general conclusion that previous announcements of the isolation of such β-forms are incorrect. The instance of the β-benzoate of B. Helferich and H. Sieber [55] is, however, an exception and the claim of these authors to have isolated the first true β-glyceride is upheld. Likewise, the assumption of αβ- and αγ-isomerism in diglycerides is shown by further cases to be based frequently on insufficient evidence. A list of apparently trustworthy methods for preparing α-, β-, αβ-, αγ-, and αβγ-esters and ethers is given.

It is pointed out that in some of the instances the cause of the production of unexpected isomerides is doubtless inherent in the syntheses themselves : for instance, the production of αβ- or αγ-ethers from both αβ- and αγ-dihalogenohydrins is probably to be attributed to intermediate αβ-oxide formation. This explanation may extend to similar preparations of the glycerol esters. Nevertheless, interchanges of acid radicals with one another, and also with different radicals, take place so easily that an explanation of these changes not involving a large or difficult movement of such heavy radicals as the stearyl and palmityl groups is needed.

If a tendency towards ortho-ester formation, as originally suggested by E. Fischer, be taken into consideration, the migration of acid radicals can be represented merely by a rearrangement of valencies in which little or no relative movement of the atoms themselves has to be presumed.



αγ-Distearin β-palmitate.



βγ-Distearin α-palmitate.

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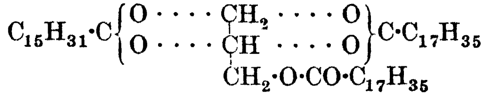
[54] A. Fairbourne, *J.*, 1930, 369; *A.*, 574.

[55] *Z. physiol. Chem.*, 1927, **170**, 31; *A.*, 1928, 44.

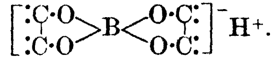
Moreover, if conditions can exist in which the Hantzsch type of carboxyl group actually occurs, the above two formulæ may become identical,



$$C_{15}H_{31}\cdot C\left\{\begin{array}{l} O\cdots\cdots CH_2\cdots\cdots O\\ O\cdots\cdots CH\;\;\cdots\cdots O \end{array}\right\}C\cdot C_{17}H_{35}$$
$$\qquad\qquad CH_2\cdot O\cdot CO\cdot C_{17}H_{35}$$

and in any case, a tendency towards the transitory formation of such αβ-oxide rings is held to be probable. On this basis the migrations which so frequently appear to take place while other reactions are in progress (*e.g.*, the migration of an acyl radical simultaneously with the elimination of a halogen atom, even if the glycerol molecule does not contain a hydroxyl group) can be explained.

The acid complexes formed between boric acid and glycols are shown by methods not involving their separation from solution to have the composition HBD_2, D representing a diol residue.[56] One such method is based on hydrogen-ion determinations in aqueous solutions of boric acid and diol in various proportions, consideration of the equilibria involved giving a relation $-\Delta p_H = (n/2)\log a$, connecting the difference of p_H of two solutions and the ratio a of the amounts of diol present in each, n being the number of molecules of diol combining with 1 mol. of boric acid. A second method involves the consideration of the partition of hydroxyl ions between the acid complex and free boric acid during neutralisation, and a third depends on cryoscopic measurements. The structure and mode of ionisation of these complexes are considered to be represented by the general formula



$$\left[\begin{array}{l}:C\cdot O\\ :C\cdot O\end{array}\!\!>B<\!\!\begin{array}{l}O\cdot C:\\ O\cdot C:\end{array}\right]^{-}H^{+}.$$

A phenomenon which appears to involve the formation of ring complexes of somewhat similar character to the foregoing, and has a direct bearing on the spatial distribution of the hydroxyl groups of glycols, is revealed by the study of the solubility of arsenic compounds, particularly of arsinoacetic acid, in 99% acetic acid in the presence of various glycols.[57] It is found that two adjacent hydroxyl groups in the glycol generally increase the solubility of arsinoacetic acid, arsenic trioxide, and resorcinolarsinic acid, and this effect is intensified when three or four hydroxyl groups are in a position favourable to the formation of a five-membered ring, as in ethylene glycol, glycerol, pyrocatechol, etc. β-Glycols and *m*- and *p*-dihydric phenols have a smaller effect. Stereoisomerides with different spatial configuration of the hydroxyl groups have different effects, *e.g.*, active and *meso*-forms of tartaric acid, *cis*- and *trans*-forms of *cyclo*hexanediol. The magnitude of the effect is altered by substitution; it is increased by the introduction of alkyl groups, but the extent of increase is dependent on the number and nature of the substituents. The influence of carboxyl or carbonyl groups, *e.g.*, in succinic acid or benzil, on the solubility is small.

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[56] J. Böeseken, N. Vermaas, and A. T. Kuchlin, *Rec. trav. chim.*, 1930, **49**, 711; *A.*, 1018.

[57] B. Englund, *Svensk Kem. Tidskr.*, 1928, **40**, 278; *A.*, 1929, 52; *J. pr. Chem.*, 1929, [ii], **122**, 121; 1930, [ii], **124**, 191; *A.*, 1929, 945; 1930, 330.

Investigation of the rate of dehydration of the unsaturated glycol $CMe_2(OH){\cdot}CH{:}CH{\cdot}CMe_2{\cdot}OH$ in water in the presence of hydrogen ions [58] shows the strong effect produced by the spatial configuration. The dehydration of the *cis*-form of the diol in solutions of mineral and organic acids is catalysed by hydrogen ions. The reaction is unimolecular and complete, the oxide being the only product. Measurements of the velocity at different temperatures, employing hydrochloric acid, show the temperature coefficient to be high, whilst comparative measurements made in different acids show that the velocity of catalysis is only approximately proportional to the hydrogen-ion concentration, increasing more rapidly than the latter. So far as the experiments show, the velocity in weakly acid media is constant, the acidity being unaffected by addition of the ditertiary glycol; in more strongly acid solution, the velocity coefficient decreases slightly but regularly as the concentration of the glycol increases. Dehydration of the *trans*-form, on the other hand, is slow, yielding not a cyclic oxide but open-chain polyolefins.

The result of replacing the hydroxyl groups in the acetylenic glycol $CMe_2(OH){\cdot}C{\vdots}C{\cdot}CMe_2{\cdot}OH$ by bromine is of interest. The change has been effected [59] with phosphorus tribromide and, in addition to a product which doubtless has the constitution $CMe_2Br{\cdot}C{\vdots}C{\cdot}CMe_2Br$, two other isomeric dibromides have been obtained. One of these appears to be the compound

$$CMe_2{:}CBr{\cdot}CBr{:}CMe_2$$

obtainable from the first on heating, or directly from the glycol by the action of hydrobromic acid; to the other dibromide, no formula has been definitely assigned, although on the basis of its oxidation products a cyclic formula has been thought to apply. Nevertheless it seems to the writer that the oxidation products, while not lending support to this suggestion, are precisely those to be expected from an allene derivative of the formula $CMe_2{:}C{:}CBr{\cdot}CMe_2Br$, both this and the isomeric diolefin being produced during, or subsequently to, replacement of hydroxyl, by anionotropic change.

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[58] M. Bourguel and R. Rambaud, *Bull. Soc. chim.*, 1930, [iv], **47**, 173; *A.*, 574.

[59] V. N. Krestinski and L. J. Bashenova-Koslovskaia, *J. Russ. Phys. Chem. Soc.*, 1929, **61**, 1691; *A.*, 1930, 574.

Various useful methods have been devised for the production of acetals and ketals from glycols, hydroxy-acids, and hydroxy-ketones. Derivatives of the enolic form of acetol have been obtained by reacting on *iso*propylideneglycerol α-monochlorohydrin with potassium hydroxide, and a dimeric derivative of the enolic form of methylglyoxal has been analogously obtained from the *p*-toluenesulphonyl derivative of glyceraldehyde methyl*cyclo*acetal;[60] the diethylacetal of hydroxyacetone is shown to be obtainable[61] if the acetol acetate is allowed to react with ethyl orthoformate and the product hydrolysed with lime, although the interaction of free acetol or acetol formate with the same reagent yields only acetol ethyl*cyclo*acetal; ethylidene derivatives of glycols and hydroxy-acids can be obtained by interaction of the latter with acetylene in the presence of a catalyst.[62] In the last reaction the catalysts employed to effect condensation are solutions of boron or silicon fluorides in alcohols with mercuric oxide. The active constituents of these solutions, which possess high electrical conductivity, are probably hydrofluoboric and hydrofluosilicic acids. The compound BF_3,Et_2O formed by dissolving boron trifluoride in ether is also stated to be efficacious as a catalyst.

An examination of the thermal decomposition of acetone in the gaseous state carried out several years ago showed that between 506° and 632° the process constitutes a homogeneous unimolecular reaction, the products of decomposition being about one-half saturated hydrocarbons and hydrogen, one-third carbon monoxide, and the remainder carbon dioxide and ethylene.[63] A new examination[64] has shown that for every 100 mols. of acetone vapour passed (with nitrogen) through a quartz tube heated in an electric furnace, approximately 60 mols. of keten can be recovered. Hence the primary reaction in the unimolecular decomposition is probably the separation of a molecule of methane and the formation of keten, which undergoes a bimolecular decomposition into ethylene and carbon monoxide at the high temperature. If this is the correct explanation, the proportions of methane, ethylene, and carbon monoxide which would then be found agree fairly closely with the previous experimental result.

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[60] H. O. L. Fischer, E. Baer, L. Feldmann, and L. Ahlström, *Ber.*, 1930, **63**, [*B*], 1732; *A.*, 1164.

[61] V. V. Evlampiev, *J. Russ. Phys. Chem. Soc.*, 1929, **61**, 2017; *A.*, 1930, 580.

[62] J. A. Nieuwland, R. R. Vogt, and W. L. Fookey, *J. Amer. Chem. Soc.*, 1930, **52**, 1018; *A.*, 745.

[63] C. N. Hinshelwood and W. K. Hutchison, *Proc. Roy. Soc.*, 1926, [*A*], **111**, 245; *A.*, 1926, 691.

[64] F. O. Rice and R. E. Vollrath, *Proc. Nat. Acad. Sci.*, 1929, **15**, 702; *A.*, 1929, 1425.

The extent of enolisation produced in a number of ketones on the addition of various organo-magnesium halides seems to bear no relation to the structure of the given ketone,[65] but, on the whole, increases with the atomic weight of the halide present in the Grignard reagent, and is greater where tertiary organic radicals are present than primary or secondary. Enolisation, using magnesium *tert.*-butyl chloride, amounts for di-*n*-butyl ketone and carvone to about 20%, for acetophenone 31%, for *cyclo*pentanone 32·5%, for thujone 41%, for 4-methyl*cyclo*hexanone 46%; for *cyclo*hexanone 50·5%, for menthone 51%, and for mesityl oxide 60%. In relation to these values *cyclo*hexanone contains originally 8·2% of enol, 4-methyl*cyclo*-hexanone 6·3%, and mesityl oxide 6·3%, whilst the remainder are normally exclusively in the keto-form. No connexion appears thus to exist between the tendency towards allelotropism of a given substance and its degree of enolisation under the influence of the Grignard reagent.

As a result of a determination of the extent of enolisation of ethyl acetoacetate and acetylacetone in alkaline solution, P. Grossmann [66] came to the conclusion that, with a considerable excess of alkali, the high results obtained corresponded with the presence of a dienol. In determining the amount of enol the usual practice of acidifying the solution before treatment with bromine was replaced by direct addition of an acid bromine solution and removal of the excess of bromine by aniline hydrochloride. The question has been re-examined by A. Hantzsch and W. Kröber,[67] who state that titration of alkaline solutions of ethyl acetoacetate and of acetylacetone with bromine solutions shows that the excess of bromine taken up by the enolic compound varies with the concentration of the bromine solution and is due to secondary reactions. Measurements of the amount of hydrogen liberated by the action of acetylacetone and of benzoylacetone on sodium or potassium suspended in benzene or xylene show that only one atom of the alkali metal is taken up by the enol. The formula $\mathrm{COMe{\cdot}CH{:}C(ONa){\cdot}OEt}$ for ethyl sodioacetoacetate and the existence of dienol salts with the group $\mathrm{{\cdot}C(ONa){:}C{:}C(ONa){\cdot}}$ proposed by Grossmann are considered to be incorrect.

Distillation of free ethyl acetoacetate at the ordinary temperature and 10^{-5} mm. pressure in quartz or Pyrex, but not in soft, glass vessels, has yielded fractions containing 30—40% of the enol, the half-life period of which is about 500 hours.[68] These are approximately ten times as stable as any previously obtained. No substance has, however, been found capable of stabilising the product and attempts to increase the stability by removing traces of water with silica gel or acetyl chloride proved unsuccessful. In this connexion it is of interest that dimethylpyruvic acid as obtained by distillation at atmospheric pressure is the pure keto-form; when this is dissolved in water, an equilibrium between enolic and ketonic forms is obtained, a $1{\cdot}0M$-solution containing 0·47%, a $0{\cdot}1M$-solution 0·28%, and a $0{\cdot}01M$-solution only a trace of the enolic form.[69] After addition of a small amount of alkali a third form is reported to be detectable spectrographically.

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[65] V. Grignard and H. Blanchon, *Rocz. Chem.*, 1929, **9**, 547; *A.*, **1930**, **67**.

[66] *Z. physikal. Chem.*, 1924, **109**, 305; *A.*, 1924, i, 834.

[67] *Ibid.*, 1930, **147**, 293; *A.*, 1021.

[68] F. O. Rice and J. J. Sullivan, *J. Amer. Chem. Soc.*, 1928, **50**, 3048.

Bromomalondialdehyde behaves in aqueous solution as a true acid.[70] In alcohol the keto–enol equilibrium, as determined by K. Meyer's bromination method, is established only after 48 hours and corresponds with 24% of the enol at the ordinary temperature. A rise in temperature raises the proportion of the enol.

The sodium salts of acetone, methyl propyl ketone, camphor, and fenchone have been prepared by the action on the ketones of sodium in liquid ammonia; benzophenone yields with sodamide and potassamide the compounds $C_{13}H_{10}O,NaNH_2$ and $C_{13}H_{10}O,NK_3$, respectively.[71]

The possibility of synthesising *cis*- and *trans*-forms of *n*-alkylideneacetones has been demonstrated in the instance of butylideneacetone.[72] The two forms of this αβ-unsaturated ketone resist configurational change and interconversion has been effected only in the direction of *cis* ⟶ *trans*, through the hydrobromide. The self-additive tendency of these substances in the presence of alkaline reagents has not permitted examination of the relationship existing between geometrical configuration and αβ,βγ-isomerisation, but it has been possible by the action of dilute acid to convert the corresponding βγ-ketone into a mixture of *cis* and *trans* αβ-forms.

Optimum conditions for the condensation of ketones by hydrogen chloride are obtained when the molecular ratio of acid to ketone is 2 : 3.[73] It is a notable fact that with the exception of methyl ethyl ketone reaction in the presence of this condensing agent is confined to the ketone group of one molecule and the methyl group of the second molecule. Methyl ethyl ketone suffers condensation (in conformity with former results for an acid condensing agent) at the ethyl group of the second molecule, yielding γ-chloro-γδ-dimethylhexan-β-one. This gives with alkali the corresponding ketone, CMeEt:CMe·COMe. If hydrogen chloride be replaced by hydrogen bromide or hydrogen iodide in the same molecular ratio of acid to ketone, higher yields of the condensation products are obtained; moreover, the condensation of methyl ketones with secondary carbon groups, but not of ketones with tertiary groups, is facilitated.

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[69] C. Fromageot and S. Perraud, *Biochem. Z.*, 1930, **223**, 213; *A.*, 1272.

[70] J. Grard, *Compt. rend.*, 1930, **190**, 187; *A.*, 324.

[71] H. H. Strain, *J. Amer. Chem. Soc.*, 1930, **52**, 3383; *A.*, 1273.

[72] E. N. Eccott and R. P. Linstead, *J.*, 1930, 905. Compare H. Stobbe and F. J. Wilson, *Annalen*, 1910, **374**, 237; *J.*, 1910, **97**, 1722.

[73] V. Grignard and J. Cologne, *Compt. rend.*, 1930, **190**, 1349; *A.*, 1022.

Carbohydrates.

The synthesis of 2 : 3 : 4 : 5 : 6-penta-acetyl glucose, a true open-chain aldehyde form of a sugar,[74] has been followed by the synthesis of several analogous compounds. Penta-acetyl galactose [75] and tetra-acetyl *l*-arabinose,[76] derived from the diethylmercaptals of the appropriate sugars, have rotation values in chloroform of — 25° and — 65° respectively, showing that the carbonyl group can produce a relatively high rotation in spite of the absence of rings. Aldehydo-pentabenzoyl glucose has been obtained in an analogous manner.[77] Other notable syntheses in the monosaccharide group are those of *d*-glucoheptulose,[78] obtained by the Lobry de Bruyn rearrangement of *d*-α-glucoheptose and clearly related to the glucoheptulose of Bertrand and Nitzberg [79] as the optical antipode, *l*-threose [80] (in solution and in the form of its osazone), and *epi*fucose (*l*-talomethylose).[81]

The elucidation of the constitution of the sugar acetones has resulted in the extensive employment of the *iso*propylidene derivatives of sugars, sugar mercaptals, and sugar acids for synthetic purposes. This is exemplified in the preparation of a number of *gem*-dialkyl derivatives of *d*-galactose [82] and of fructofuranose [83] and in the synthesis of the 4-methyl derivatives of *d*-mannose [84] and *d*-galactose.[85] The dicarbonates of glucose, fructose, mannose, and arabinose, which have now been obtained as well-defined and easily characterised products,[86] will doubtless prove of equal utility, and for certain purposes, owing to their less ready hydrolysis by dilute acids to the parent sugars and their immediate attack by even cold alkali, will prove superior to the sugar-acetones. The constitutional formulæ suggested for these substances are based on the similarity in properties to the diacetones.

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[74] *Ann. Reports*, 1929, **26**, 92.

[75] M. L. Wolfrom, *J. Amer. Chem. Soc.*, 1930, **52**, 2464; *A.*, 1023.

[76] M. L. Wolfrom and M. R. Newlin, *ibid.*, p. 3619; *A.*, 1411.

[77] P. Brigl and H. Mühlschlegel, *Ber.*, 1930, **63**, [*B*], 1551; *A.*, 1022.

[78] W. C. Austin, *J. Amer. Chem. Soc.*, 1930, **52**, 2106; *A.*, 894.

[79] *Compt. rend.*, 1928, **186**, 925, 1172, 1773; *A.*, 1928, 510, 620, 867.

[80] V. Deulofeu, *J.*, 1929, 2458; *A.*, 1930, 68.

[81] E. Votoček and V. Kučerenko, *J. Czech. Chem. Comm.*, 1930, **2**, 47; *A.*, 325.

[82] H. Ohle and C. Dambergis, *Annalen*, 1930, **481**, 255; *A.*, 1274.

[83] H. Ohle and O. Hecht, *ibid.*, p. 233; *A.*, 1274.

[84] E. Pacsu and C. von Kary, *Ber.*, 1929, **62**, [*B*], 2811; *A.*, 1930, 70.

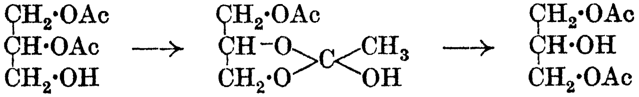
[85] E. Pacsu and A. Löb, *ibid.*, p. 3104; *A.*, 1930, 197.

[86] W. N. Haworth and C. R. Porter, *J.*, 1930, 151; *A.*, 326.

Formulation of Sugars.—A considerable amount of new work relating to the representation of the sugars as pyranose and furanose ring-structures has been carried out. This includes the isolation of missing forms in one or other series, and the investigation of the comparative stability and optical rotatory powers of representatives of both series. New lactones of *l*-rhamnonic acid [87] and 2 : 3 : 4-trimethylrhamnonic acid [88] have been isolated, the former of which probably, and the latter more certainly, has the pyranose structure of a true δ-lactone; α-methylmannofuranoside, tetramethylmannofuranose,[89] trimethyl-lyxofuranoside, and trimethyl-lyxofuranose [90] have also been obtained and found to resemble closely other γ-sugar derivatives.

Although representatives of the two types of ring-structure show a large difference in the ease of oxidation by permanganate in the presence of an acid phosphate buffer,[91] yet an attempt to estimate the comparative stability of pyranose and furanose sugar derivatives has met with only slight success; [92] observations relating to the differential absorption of ultra-violet light by the two types of ring structure have disclosed only very slight spectrographic differences.[93]

Various examples are known of the wandering of acyl groups linked with polyhydric alcohol residues. One of the first to observe the change was E. Fischer,[94] who suggested that the migration mechanism might be explained by the intermediate formation of an ortho-carbonic ester group in the manner :



$$\begin{array}{l}CH_2\cdot OAc\\ CH\cdot OAc\\ CH_2\cdot OH\end{array} \longrightarrow \begin{array}{l}CH_2\cdot OAc\\ CH-O\\ CH_2\cdot O\end{array}\!\!>C<\!\!\begin{array}{l}CH_3\\ OH\end{array} \longrightarrow \begin{array}{l}CH_2\cdot OAc\\ CH\cdot OH\\ CH_2\cdot OAc\end{array}$$

The adoption of Fischer's explanation has been shown to provide a way [95] not only of representing the simple migration of acetyl as illustrated in the conversion of 3- into 6-monoacetyl glucose derivatives [96] but also of relating 1 : 2 : 3 : 4-tetra-acetyl β-glucose (I) [97] and 2 : 3 : 4 : 6-tetra-acetyl β-glucose (II) [98] to the supposed 1 : 2 : 3 : 6-tetra-acetyl glucose of B. Helferich and W. Klein.[99] There is definite evidence for the view that the supposed 1 : 2 : 3 : 6-tetra-acetyl glucose which is formed from, and is known to exist in equilibrium with, (I) in alkaline solution represents the cyclic intermediate form (III) produced during the migration of an acetyl group from the position C_1 to C_6 in the carbon chain of (I) when the latter is alkylated with methyl iodide and silver oxide. The final product so obtained is the methyl glucoside (IV) corresponding to, and derivable from, (II).

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[87] E. L. Jackson and C. S. Hudson, *J. Amer. Chem. Soc.*, 1930, **52**, 1270; *A.*, 744.

[88] J. Avery and E. L. Hirst, *J.*, 1929, 2466; *A.*, 1930, 68; F. E. Wright, *J. Amer. Chem. Soc.*, 1930, **52**, 1276; *A.*, 744.

[89] W. N. Haworth, E. L. Hirst, and J. I. Webb, *J.*, 1930, 651; *A.*, 748.

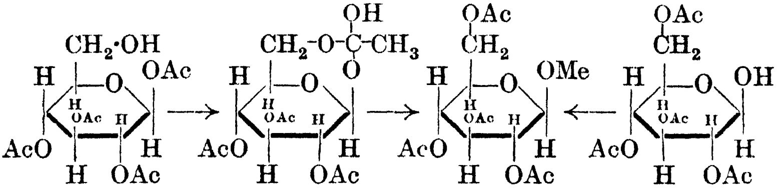
[90] H. G. Bott, E. L. Hirst, and J. A. B. Smith, *ibid.*, p. 658; *A.*, 747.

[91] C. H. Whitnah and J. E. Milbery, *J. Amer. Chem. Soc.*, 1930, **52**, 1627; *A.*, 748.

[92] H. Ohle and V. Marecek, *Ber.*, 1930, **63**, [*B*], 612; *A.*, 581.

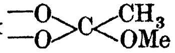
[93] F. Goos, H. H. Schlubach, and G. A. Schröter, *Z. physiol. Chem.*, 1930, **186**, 148; *A.*, 455.

[94] *Ber.*, 1920, **53**, 1624; *A.*, 1920, i, 808.



(I.) (III.) (IV.) (II.)

The migration of the 4- rather than the 1-acetyl group, as was originally suggested, is not finally excluded,[1] but would seem to be unlikely in view of the fact that a further transposition of acetyl residues must then occur when the resultant compound undergoes conversion into 2 : 3 : 4 : 6-tetra-acetyl β-methylglucoside (IV).

A similar explanation has been applied to the formation of the anomalous third (" γ ") forms of triacetyl methylrhamnoside, tetra-acetyl methylmannoside, and hepta-acetyl chloromaltose.[2] The existence of the first of these had been tentatively explained by assuming a novel form of stereoisomerism; [3] now, however, the resistance to hydrolysis of one of the four acetyl groups in this compound—the feature distinguishing it from the two already known triacetyl methylrhamnosides (α- and β-forms)—is attributed to its participation in the complex  $\begin{matrix}-\mathrm{O}\\-\mathrm{O}\end{matrix}\!\!>\!\mathrm{C}\!<\!\!\begin{matrix}\mathrm{CH_3}\\\mathrm{OMe}\end{matrix}$. According to the new explanation, which receives some support from absorption measurements,[4] the third or obstructed varieties of the three compounds are to be represented thus :

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[95] W. N. Haworth, E. L. Hirst, and E. G. Teece, *J.*, 1930, 1405; *A.*, 1022.

[96] K. Josephson, *Ber.*, 1929, **62**, [*B*], 317, 1913; *A.*, 1929, 428, 1278; *Annalen*, 1929, **472**, 217; *A.*, 1929, 1044; *Svensk Kem. Tidskr.*, 1929, **41**, 99; *A.*, 1929, 912.

[97] J. W. H. Oldham, *J.*, 1925, **127**, 2840; *A.*, 1926, 151.

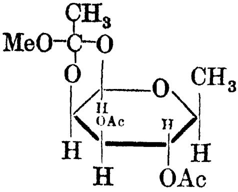
[98] E. Fischer and K. Delbrück, *Ber.*, 1909, **42**, 2778; *A.*, 1909, i, 633.

[99] *Annalen*, 1927, **455**, 173; *A.*, 1927, 858.

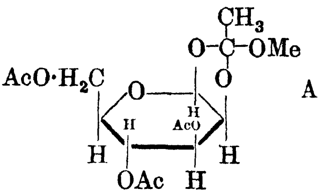
[1] Compare B. Helferich, *Ber.*, 1930, **63**, [*B*], 2142; *A.*, 1411.

[2] H. G. Bott, W. N. Haworth, and E. L. Hirst, *J.*, 1930, 1395; *A.*, 1024; K. Freudenberg, *Naturwiss.*, 1930, **18**, 393; *A.*, 894; K. Freudenberg and H. Scholz, *Ber.*, 1930, **63**, [*B*], 1969; *A.*, 1412.

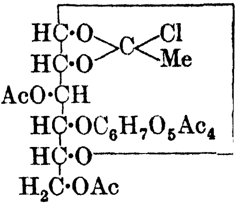
[3] W. N. Haworth, E. L. Hirst, and E. J. Miller, *J.*, 1929, 2469; *A.*, 1930, 68.



Third form of triacetyl methylrhamnoside.



Third form of tetra-acetyl methylmannoside.



Third form of hepta-acetyl chloromaltose.

It is contended by C. S. Hudson that change of ring form may and does occur during the methylation of sugars, a circumstance held to vitiate certain of the conclusions of W. N. Haworth with respect to the structural representation of the sugars. New formulæ deduced by applying the principle of optical superposition to available optical data have accordingly been put forward for various mono- and poly-saccharides.[5] Quite apart, however, from the coherence of the chemical evidence which supports the existing formulation, there is important new evidence that the principle of optical superposition does not apply uniformly throughout the sugar group.[6] In the fructose series, for example, difficulties are encountered in applying Hudson's methods,[7] since the differences in the activities of the α-series in different solvents are unusually great, whereas smaller differences are observed in the β-series : hence the magnitude of the increment depends greatly on the choice of solvent and it is concluded from the data obtained for a variety of solvents that the increments calculated from the values of the aldose series cannot be applied in the ketose series, in which the values are markedly higher. The limitations to the usefulness of the optical method in diagnosing constitution also appear from a study of derivatives of 5-*p*-toluenesulphonyl-3 : 6-anhydroglucose [8] and from other observations.[9]

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[4] E. Braun, *Naturwiss.*, 1930, **18**, 393; *A.*, 895; *Ber.*, 1930, **63**, [*B*], 1972; *A.*, 1411.

[5] *J. Amer. Chem. Soc.*, 1930, **52**, 1680, 1707; *A.*, 747.

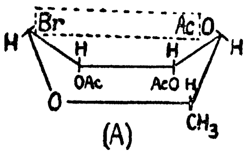
[6] W. N. Haworth, *Nature*, 1930, **126**, 238; *A.*, 1273; *J. Amer. Chem. Soc.*, 1930, **52**, 4169.

[7] H. H. Schlubach and G. A. Schröter, *Ber.*, 1930, **63**, [*B*], 364; *A.*, 456.

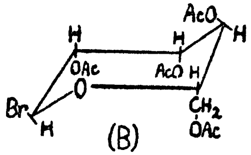
[8] H. Ohle and E. Euler, *ibid.*, p. 1796; *A.*, 1165.

[9] F. Micheel, *ibid.*, p. 347; *A.*, 455; H. H. Schlubach and R. Gilbert, *ibid.*, p. 2292; *A.*, 1412.

From measurements of the rotation of α- and β-glucose and α-methylglucoside in borax solutions [10] it appears that the glucosidic and 2-carbon hydroxyl groups are essential for the reaction with borate, and occupy in α-glucose *cis*-positions. A means of determining directly the configuration of α- and β-forms in the sugar series has been sought, and consistent results have been obtained in connecting the reactivity of a number of glucosyl halides towards trimethylamine with the *cis*- or *trans*-configuration of the substituent groups at the 1- and 2-carbon atoms of the chain.[11] Only a *cis*-relationship of these groups would seem to permit of quaternary salt formation with the amine, but the method is not generally applicable in this simple form, since the interaction of acetobromo-*l*-rhamnose with trimethylamine is found to lead to the production of a diacetyl anhydrorhamnose. On the assumption that Walden inversion does not occur at the C_1-atom during ring closure the anhydride ring is regarded as produced by the removal of bromine along with the 4-acetyl group, a procedure which may be rendered possible by the approach in space of the two groups in a folded phase of the pyran ring (formula A). It is suggested that the corresponding stability of acetobromomannose towards trimethylamine may be due to the greater distance of the bromine atom from the 4-acetyl group as indicated in formula B.



(A)



(B)

Further progress has been made in the investigation of two naturally occurring sugars, digitoxose, and hamamelose (hamamelihexose). To the former, which had been shown by H. Kiliani [12] to be a 2 : 6-deoxyhexose, a formula has been assigned : [13] for the latter, obtained as methylhamameloside from the hamameli-tannin described by Freudenberg and Blümmel,[14] a branched-chain formula different from that originally suggested by the latter authors has been advanced.[15]

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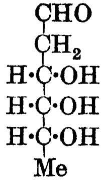
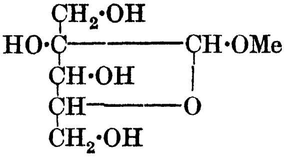
[10] M. Levy, *J. Biol. Chem.*, 1929, **84**, 749, 763; *A.*, 1930, 69.
[11] F. Micheel and H. Micheel, *Ber.*, 1930, **63**, [*B*], 386; *A.*, 455.
[12] *Ber.*, 1922, **55**, [*B*], 75; *A.*, 1922, i, 224.
[13] F. Micheel, *Ber.*, 1930, **63**, [*B*], 347; *A.*, 455.
[14] *Annalen*, 1924, **440**, 45; *A.*, 1925, i, 51.
[15] O. T. Schmidt, *Annalen*, 1929, **476**, 250; *A.*, 1930, 197.



$$\begin{array}{c} CHO \\ | \\ CH_2 \\ | \\ H\cdot C\cdot OH \\ | \\ H\cdot C\cdot OH \\ | \\ H\cdot C\cdot OH \\ | \\ Me \end{array}$$

Digitoxose.



Methylhamameloside.

The probability that a genetic relationship explains the existence together in natural products of sugars and of pyran or pyrone nuclei[16] is increased by a demonstration of the convertibility of acetobromoglucose and acetobromogalactose into tetra-acetyl 2-hydroxyglucal and tetra-acetyl 2-hydroxygalactal respectively, and thence smoothly into diacetylkojic acid.[17]

Synthetic Glucosides.—The nature of the reagents employed to effect the conversion of glucosyl halides into alkyl glucosides would appear to determine, to some extent at least, the α- or the β-form of the product. It is possible to obtain either an α- or a β-methylglucoside from both 2-trichloroacetyl-3 : 4 : 6-triacetyl-β-glucosyl chloride and 3 : 4 : 6-triacetyl-β-glucosyl chloride by selecting appropriate conditions. This may be due to each reagent having its own isomerising effect, but it is considered to be more probable that the first stage in these processes consists in the addition of the reagent to the glucosyl halide and that the subsequent behaviour of the additive compound so obtained is determined by the nature of the reacting systems.[18] Direct conversion of β- into α-glucosides has been found to result from the action of titanium tetrachloride in chloroform,[19] and α-alkylglucosides admixed only with minor proportions of the corresponding β-forms have been obtained by heating the dibenzylmercaptals of the aldomonoses with mercuric chloride dissolved in the requisite alcohol.[20]

It has now been established that dihydroxyanthraquinone diglucosides, including such as contain the sugar residues attached to the same benzene nucleus, can exist.[21] The preparation of an alizarin diglucoside should therefore be possible. α-Hydroxyl groups, when protected by β-hydroxyl groups, cannot be caused to react with halogeno-sugars by using an excess of the latter, by prolonging the reaction, or by raising the temperature. It appears possible, therefore, that ruberythric acid is a monobioside, but owing to the demonstrated difference of its octa-acetyl derivative from that of an octa-acetyl maltoside derived synthetically from alizarin it is apparently not a maltoside. Rubiadin glucoside has now been shown definitely by synthesis to be 3-β-glucosidoxy-1-hydroxy-2-methylanthraquinone.[22]

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[16] W. N. Haworth, " Constitution of Sugars," p. 38.

[17] K. Maurer, *Ber.*, 1930, **63**, [*B*], 25; *A.*, 326; K. Maurer and A. Müller, *ibid.*, p. 2069; *A.*, 1412.

[18] W. J. Hickinbottom, *J.*, 1930, 1338; *A.*, 1023.

[19] E. Pacsu, *J. Amer. Chem. Soc.*, 1930, **52**, 2563; *A.*, 1023.

[20] E. Pacsu and N. Ticharich, *Ber.*, 1929, **62**, [*B*], 3008; *A.*, 1930, 197.

[21] A. Müller, *ibid.*, p. 2793; *A.*, 1930, 71; A. Robertson, *J.*, 1930, 1136; *A.*, 895.

Di- and Tri-saccharides.

In supplementing the evidence furnished by methylation methods as to the correct formulation of disaccharides, use has been made of the 1 : 2- and 5 : 6-unsaturated derivatives of sugars (glucals and glucoseens). Thus new evidence in favour of the C_6-linking of the components in melibiose is provided by the behaviour of melibial taken in conjunction with the capacity of the sugar to form both 1 : 4- and 1 : 5-glucosides and lactones.[23] New evidence as to the manner of coupling and the pyranose ring structure of trehalose is likewise afforded by the formation of a bis-triphenylmethane derivative of this sugar and of a non-reducing trehalosediene which is hydrolysable to *iso*rhamnonose.[24]

Gentiobial, a new compound of the glucal class, has been shown to yield a mixture of hydroglucal and glucose when submitted to the action of emulsin after reduction.[25] It is considered, therefore, to be a 6-glucosidoglucal, the glucal structure containing a pyran ring. Analogously, the already known cellobial and lactal are considered to be 4-glucosidoglucose and 4-galactosidoglucal respectively. Glucal itself passes rapidly on oxidation with perbenzoic acid to mannose,[26] which fact corresponds with an earlier observation of M. Bergmann and his collaborators that lactal yields 4-galactosidomannose with the same reagent.[27] It has been found, however, that 3-methyl glucal yields 3-methyl glucose with perbenzoic acid [28] and that the 4-galactosidomannose from lactal is a mixture of at least two sugars.[29]

A new disaccharide ketose has been derived from α-lactose by the

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[22] E. T. Jones and A. Robertson, *J.*, 1930, 1699; *A.*, 1167.

[23] P. A. Levene and E. Jorpes, *J. Biol. Chem.*, 1930, **86**, 403; *A.*, 749.

[24] H. Bredereck, *Ber.*, 1930, **63**, [*B*], 959; *A.*, 748.

[25] M. Bergmann and W. Freudenberg, *ibid.*, 1929, **62**, [*B*], 2783; *A.*, 1930, 70.

[26] C. Tanaka, *Bull. Chem. Soc. Japan*, 1930, **5**, 214; *A.*, 1273.

[27] *Annalen*, 1923, **434**, 79; *A.*, 1924, i, 265.

[28] P. A. Levene and A. L. Raymond, *J. Biol. Chem.*, 1930, **88**, 513; *A.*, 1411.

[29] A. J. Watters and C. S. Hudson, *J. Amer. Chem. Soc.*, 1930, **52**, 3472; *A.*, 1275.

Lobry de Bruyn method. This substance, *d*-lactulose,[30] which yields *d*-fructose and *d*-galactose on hydrolysis, is considered to be 4-β-*d*-galactosido-α-*d*-fructose.

In connexion with the synthesis of sucrose, recent condensations of tetra-acetyl γ-fructose with tetra-acetyl glucose have yielded octa-acetyl *iso*sucrose as the only crystallisable product (occasionally octa-acetyl *iso*trehalose is isolated).[31] As *iso*sucrose is less stable than sucrose, it is improbable that octa-acetyl sucrose is first formed. The isolation of two varieties of octa-acetyl sucrose which have the same optical rotation in chloroform but different melting points has been reported.[32] These do not correspond with the " A " and " B " varieties of sucrose but are considered to be stable and labile forms.

The investigation of several natural products has proceeded a stage further. From the calcium aldobionate obtained by hydrolysis of gum arabic, a crystalline aldobionic acid has been isolated which yields a dicarboxybionic acid on oxidation. The fission products of both acids confirm the view that the aldobionic acid is a glycuronogalactose and the slow rate of hydrolysis of the two methylglucosides derived from the aldobionic acid shows that both of these possess the pyranose structure.[33] The aldobionic acid is therefore regarded as glycurono-3(or 6)-α-galactose.

The third sugar constituent of scammonin has been recognised as rhodeose, which remains together with rhamnose when the hydrolysis product of scammonin is fermented to remove glucose.[34] The sugar of α-crocin when acetylated yields a product which is found to be identical with octa-acetyl gentiobiose.[35]

Acid hydrolysis of the glucomannan obtainable from " konjak powder " (powdered tubers of *Amorphophallus konjak*, C. Koch) confirms the view that this polysaccharide contains mannose and glucose in the ratio of 2 : 1.[36] Glucomannan gives a triacetate and yields by acetolysis a mixture from which glucomannotriose, glucomannobiose, and mannobiose may be obtained by deacetylation. On hydrolysis the triose yields two molecules of mannose and one molecule of glucose; similarly, glucomannobiose yields equal quantities of mannose and glucose, but mannobiose yields mannose only.

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[30] E. M. Montgomery and C. S. Hudson, *J. Amer. Chem. Soc.*, 1930, **52**, 2101; *A.*, 894.

[31] (Sir) J. C. Irvine and J. W. H. Oldham, *ibid.*, 1929, **51**, 3609; *A.*, 1930, 197.

[32] A. Pictet, *Helv. Chim. Acta*, 1930, **13**, 698; *A.*, 1166.

[33] M. Heidelberger and F. E. Kendall, *J. Biol. Chem.*, 1929, **84**, 639; *A.*, 1930, 66.

[34] E. Votoček and F. Valentin, *J. Czech. Chem. Comm.*, 1929, **1**, 606; *A.*, 1930, 71.

[35] P. Karrer and K. Miki, *Helv. Chim. Acta*, 1929, **12**, 985; *A.*, 1929, 1427.

[36] K. Nishida and H. Hashima, *J. Dept. Agric. Kyushu*, 1930, **2**, 277; *A.*, 1413.

Polysaccharides.

Uncertainty as to the trustworthiness of the cryoscopic method for the determination of the true molecular weights of the polysaccharides and their derivatives enhances the interest attached to the investigation of the relationship between viscosity and molecular condition. This relationship is the subject of a series of papers by H. Staudinger and his collaborators,[37] the theoretical considerations developed being based on the following hypotheses. (1) Variation in the specific viscosity, $\eta_{\mathrm{sp.}}$, of a colloidally dissolved substance with pressure is an indication of structure in solution which may be caused by the presence of macromolecules in such concentration that they are mutually impeditive. (2) The specific viscosity of the macromolecular hydrocarbons increases proportionately with the concentration in dilute solution but more rapidly than the concentration in concentrated sol solution and in the region of gel solution. (3) Approximate constancy in the specific viscosity of a solution over a considerable range of temperatures is evidence of the presence of macromolecules in solution and against that of strongly solvated micelles. (4) Measurements of viscosity in different solvents afford evidence of the influence of the medium on the macromolecules.

Several polysaccharides and their derivatives have been examined experimentally and the deductions from the viscosity of their solutions are referred to in the sections below.

Inulin and Lichenin.—It has been reported that the molecular weight of inulin in liquid ammonia and in molten acetamide is in agreement with the formula $(C_6H_{10}O_5)_2$ and that the isolation of the polymerised product from the latter mixture yields an inulan of composition $(C_6H_{10}O_5)_2$ which is freely soluble in water but becomes as insoluble in cold water as inulin on keeping. Observations of a similar kind have been recorded with respect to the depolymerising action on inulin of glycerol,[38] acetamide [39] and formamide,[40] but the reality of the alleged depolymerisation is denied by E. Berner.[41] This author suggests that specimens of inulin and other polysaccharides of apparently low molecular weight (determined cryoscopically) may be obtained by treatment with glycerol or ethylene glycol at the ordinary temperature, but attributes the observed effect to a physico-chemical process caused by the adsorption by the polysaccharide of appreciable quantities of the " depolymerising " and precipitating media, whereby water solubility is conferred. The adsorbed materials may only be removed by protracted heating in a vacuum.

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[37] H. Staudinger and R. Nodzu, *Ber.*, 1930, **63**, [*B*], 721; *A.*, 571; H. Staudinger and W. Heuer, *ibid.*, p. 222; *A.*, 333; H. Staudinger, K. Frey, R. Signer, W. Starek, and G. Widmer, *ibid.*, p. 2308; *A.*, 1415; H. Staudinger and O. Schweitzer, *ibid.*, p. 2317; *A.*, 1414.

[38] H. Vogel, *Ber.*, 1929, **62**, [*B*], 2980; *A.*, 1930, 198; H. H. Schlubach and H. Elsner, *ibid.*, 1930, **63**, [*B*], 362; *A.*, 456.

[39] J. Reilly and P. P. Donovan, *Sci. Proc. Roy. Dublin Soc.*, 1930, **19**, 409; *A.*, 896.

[40] H. Pringsheim and W. G. Hensel, *Ber.*, 1930, **63**, [*B*], 1096; *A.*, 896.

[41] E. Berner, *ibid.*, pp. 1356, 2760; *A.*, 1025.

The correctness of this conclusion is contested by H. H. Schlubach [42] and H. Pringsheim [43] and their collaborators and it is pointed out by the former that inulin, when treated wth benzamide, yields a product which is separable into two portions of different specific rotation; also the values recorded by different workers for the specific rotation of depolymerised products are such as to permit the products to be divided into two groups, (1) those which have the same specific rotations as the initial inulin, into which they can be transformed, and (2) those which differ in specific rotation from the original material and are not capable of spontaneous reconversion.

Viscosity measurements [44] of inulin dissolved in formamide show that its behaviour differs greatly from that of polystyrene or balata solutions. Since $\eta_{\text{sp.}}$ is much greater at lower than at higher temperatures, a change in the structure of the colloidal particles is held to occur, which is attributed to alteration of the co-ordinate linkings of the molecules among themselves and with the solvent; these changes are reversible, since particles of the original size result when the solutions are cooled.

Examination of solutions of lichenin in formamide shows the solute to be present in the molecular form at great dilution. In the more concentrated solutions co-ordinative union is considered to exist between solvent and solute and between the molecules of solute; the latter linkings are resolved when the temperature is raised and for this reason a more pronounced fall in viscosity is observed than in more dilute solutions, in which only the co-ordinative linkings between solute and solvent are ruptured. The molecular weight of lichenin is markedly higher than that of inulin; the chain appears to contain about 300 unit molecules.

Starch.—The experimental conditions necessary for effecting a sharp separation of the two main constituents of potato starch have been investigated.[45] The α-amylose from the outer envelope of the grains forms 84 ± 1% of the original starch; the β-amylose from the interior of the grains constitutes within 1% the remainder of the starch. The properties of these preparations are described and it is suggested that the great difference in the temperature coefficients of the rotations of the two components probably accounts for the divergent values previously recorded.

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[42] H. H. Schlubach and H. Elsner, *Ber.*, p. 2302; *A.*, 1415.

[43] H. Pringsheim, J. Reilly, W. G. Hensel, W. Burmeister, P. P. Donovan, and N. Hayes, *ibid.*, p. 2636.

[44] H. Staudinger and O. Schweitzer, *ibid.*, p. 2317; *A.*, 1414.

[45] M. E. Baldwin, *J. Amer. Chem. Soc.*, 1930, **52**, 2907; *A.*, 1167.

Products having the characteristics of Pringsheim's amylobiose and amylotriose have been obtained from amylose and amylopectin, respectively, by the action of cold concentrated hydrochloric acid [46] as described by this worker and his collaborators. Evidence is furnished to show that they are not definite compounds and their properties are quite inconsistent with the formulæ assigned to them.[47] Products of similar character are stated to be obtainable by the action of cold hydrochloric acid on glycogen and on glucose.

Viscosity measurements carried out on solutions of potato starch or soluble starch in formamide [44] reveal a behaviour differing completely from that of polystyrenes and caoutchouc and markedly from that of lichenin. Since even dilute solutions do not obey the Hagen–Poiseuille law, deductions concerning molecular weight are inadmissible. Freely mobile colloid molecules are absent. The specific viscosity diminishes with rise in temperature, the starch suffering change. Since the $\eta_{sp.}/c$ values in quite dilute solutions of differing concentration are not constant, irregular changes in the structure appear to occur; it cannot therefore be determined whether macromolecules are present in solution under definite conditions. It is thought probable that the colloidal particles of starch are composed of associations of extremely unstable, readily cracked molecules, and that the solution contains molecular aggregates (micelles) and not macromolecules.

Cellulose.—All the isolable products of the degradation of cellulose acetates reduce alkaline iodine solution and the iodine consumption is stated to be an accurate and reproducible measure of the free aldehydic groups and the molecular weight of the compounds.[48] Technical cellulose acetate has been further degraded with hydrogen bromide in glacial acetic acid, and the product separated by hot methyl alcohol into two portions, acetylsaccharides A and B. The iodine numbers of the respective materials indicate the presence in them of mixtures of polysaccharides containing as an average 8 and 9—11 hexose units. The product obtained by the acetolysis of cellulose according to the method of K. Hess and H. Friese[49] has been separated into a number of fractions which appear to contain 8—13 hexose residues.

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[46] R. Weidenhagen and A. Wolf, *Z. Ver. deut. Zucker-Ind.*, 1930, **80**, 265; *A.*, 1168.

[47] Compare *Ber.*, 1926, **59**, [*B*], 991, 996, 1001; *A.*, 1926, 715.

[48] M. Bergmann and H. Machemer, *ibid.*, 1930, **63**, [*B*], 316; *A.*, 457. Compare R. Willstätter and G. Schudel, *ibid.*, 1918, **51**, 780; *A.*, 1918, ii, 461.

To the latter substance, the hexa-acetyl biosan considered by Hess and Friese to be a true dimeride of the fundamental cellulose molecule, a molecular weight of 554—587 has recently been assigned[50]: this value, determined in acetic acid, is considered to be a true one, although the behaviour of different samples of acetone-soluble cellulose acetate in acetic acid is irregular and the relationship of cellulose acetate to glacial acetic acid apparently complex. The value is rejected by other workers[51] on the grounds of the unsuitability of the cryoscopic method for determining the (very large) molecular weight of this substance and of the demonstrable non-homogeneity of the biosan acetate.

With regard to the more complex acetolysis products of cellulose, the terminal groups form so small a proportion of the molecule that their accurate determination by the iodine method is held to be impossible;[52] nevertheless, on the basis of iodine consumption, the chain in cellulose itself has been computed to contain 50 glucose residues on an average as against 25—30 such residues in the starch molecule.[53]

The course of degradation of the cellulose molecule on heating with acetic acid and zinc chloride has been followed by viscosity measurements.[32] Degradation of the initial cellulose molecule occurs very rapidly, but the simpler products are much more resistant. The initial, highly viscous solutions are computed to contain cellulose triacetates of average degree of polymerisation 60—100; after 20 hours' action, the degree is reduced to 10. At the ordinary temperature, reaction proceeds extremely slowly, giving products of a degree of polymerisation 150. After 7 days at 30°, the degree is 130 and after 10 days it is 100. Since native cellulose is more highly polymerised than the most complex of its acetates, its molecular weight is considered to be above 24,000, and the cellulose molecule probably contains a chain of 500—1000 glucose residues, thus having dimensions similar to those of the caoutchouc molecule.

The simpler cellulose acetates dissolve without swelling to give mobile solutions, the viscosity of which increases proportionally to the concentration; slightly degraded cellulose acetates swell very markedly, their viscosity in solution increasing far more rapidy than the concentration, so that very viscous solutions can be obtained at relatively high dilution. In them, the total region of the macromolecules is greater than the available volume in relatively dilute solution. In place of sols in which the macromolecules have free movement, these viscous solutions correspond to gels in which the macromolecules impede one another. A 10-triacetylcelloglucan diacetate, $OAc[C_6H_7O_5Ac_3]_{10}Ac$, is stated to behave in solution like a simple substance and the gel condition is not reached until the concentration attains 22%; with a 150-triacetylcelloglucan diacetate the transition between sol and gel lies at 1·4%.

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[49] *Annalen*, 1926, **450**, 40; *A.*, 1927, 44.

[50] K. Hess, *Ber.*, 1930, **63**, [*B*], 518; *A.*, 456.

[51] K. Freudenberg, E. Bruch, and H. Rau, *ibid.*, 1929, **62**, [*B*], 3078; *A.*, 1930, 198; K. Freudenberg and E. Bruch, *ibid.*, 1930, **63**, [*B*], 535; *A.*, 457; K. H. Meyer and H. Hopff, *ibid.*, 1930, **63**, [*B*], 790; *A.*, 750.

[52] H. Staudinger and H. Freudenberger, *ibid.*, p. 2331; *A.*, 1416.

[53] K. Freudenberg, W. Kuhn, W. Dürr, F. Bolz, and G. Steinbrunn, *ibid.*, p. 1510; *A.*, 1025.

According to further indications afforded by viscosity measurements[44] cellulose triacetate in *s*-tetrachloroethane and *m*-cresol appears to form associations of molecules in concentrated solution which become resolved when the temperature is raised. In dilute solution the change of the colloidal particles is uniform and is held to be attributable to a loosening of the co-ordinative linkings between the macromolecules and those of the solvent. Since with cellulose acetate, lichenin, and inulin, as with the highly complex hydrocarbons, the specific viscosity of the solutions is the same at different temperatures, the identity of the colloidal particles with the macromolecules is regarded as established. Dibenzylcellulose exhibits abnormal behaviour in *s*-tetrachloroethane, whilst methylcellulose (OMe = 38%) shows still more marked divergence from the Hagen–Poiseuille law, in the same solvent. With cellulose nitrate, the measurements of viscosity are particularly difficult to interpret, since mechanical treatment of the solution causes greater mobility.

E. H. FARMER.

PART II.—HOMOCYCLIC DIVISION.

The Pinacol–Pinacolin and Related Rearrangements

(compare *Ann. Reports*, 1923, **20**, 115; 1925, **22**, 116; 1928, **25**, 134).

DURING the last few years a considerable volume of work has appeared dealing with the pinacol–pinacolin change and the related rearrangements of the substituted ethylene oxides and of the αβ-amino-alcohols.[1–55, 60, 61] Many data have been collected and repeated attempts have been made to enunciate general rules

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[1] P. J. Montagne and S. A. Koopal, *Rec. trav. chim.*, 1910, **29**, 136, 150; *A.*, 1910, i, 323, 324.

[2] S. A. Koopal, *ibid.*, 1915, **34**, 115; *A.*, 1915, i, 693.

[3] S. Danilov, *Ber.*, 1927, **60**, [*B*], 2390; *A.*, 1928, 64.

[4] S. Danilov and E. Venus-Danilova, *Ber.*, 1926, **59**, [*B*], 377; *A.*, 1926, 519.

[5] *Idem, ibid.*, p. 1032; *A.*, 1926, 726.

[6] *Idem, Ber.*, 1927, **60**, [*B*], 1050; *A.*, 1927, 661.

[7] E. Venus-Danilova, *Ber.*, 1928, **61**, [*B*], 1954; *A.*, 1928, 1244.

[8] *Idem, J. Russ. Phys. Chem. Soc.*, 1929, **61**, 53; *A.*, 1929, 1070.

[9] M. Godchot and G. Cauquil, *Compt. rend.*, 1928, **186**, 767; *A.*, 1928, 521.

[10] M. Gomberg and J. C. Bailar, jun., *J. Amer. Chem. Soc.*, 1929, **51**, 2229; *A.*, 1929, 1067.

[11] R. Lagrave, *Ann. Chim.*, 1927, [ix], **8**, 363; *A.*, 1928, 270.

[12] L. Leers, *Bull. Soc. chim.*, 1926, [iv], **39**, 651; *A.*, 1926, 711.

[13] (Mlle.) J. Lévy, *ibid.*, 1921, [iv], **29**, 820; *A.*, 1921, i, 788.

[14] *Idem, ibid.*, 1926, [iv], **39**, 67; *A.*, 1926, 399.

[15] (Mlle.) J. Lévy and F. Gombinska, *Compt. rend.*, 1929, **188**, 711; *A.*, 1929, 555.

[16] (Mlle.) J. Lévy and R. Lagrave, *Bull. Soc. chim.*, 1927, [iv], **41**, 833; *A.*, 1927, 872.

[17] (Mlle.) J. Lévy and M. Sfiras, *Compt. rend.*, 1927, **184**, 1335; *A.*, 1927, 662.

[18] *Idem, ibid.*, 1928, **187**, 45; *A.*, 1928, 888.

[19] (Mlle.) J. Lévy and A. Tabart, *ibid.*, 1929, **188**, 402; *A.*, 1929, 448.

[20] (Mlle.) J. Lévy and P. Weill, *ibid.*, 1927, **185**, 135; *A.*, 1927, 880.

[21] R. Locquin and L. Leers, *Bull. Soc. chim.*, 1926, [iv], **39**, 655; *A.*, 1926, 711.

[22] P. Nicolle, *ibid.*, p. 55; *A.*, 1926, 382.

[23] M. Migita, *Bull. Chem. Soc. Japan*, 1928, **3**, 308; 1929, **4**, 57; *A.*, 1929, 448, 675.

[24] W. Madelung and M. Oberwegner, *Ber.*, 1927 **60** .[*B*], 2469; *A.*, 1928, 171.

[25] L. Orthner, *Annalen*, 1927, **459**, 217; *A.*, 1928, 184.

[26] A. McKenzie and W. S. Dennler, *J.*, 1926, 1596; *A.*, 1926, 834.

[27] *Idem, Ber.*, 1927, **60**, [*B*], 220; *A.*, 1927, 243.

[28] A. McKenzie and M. S. Lesslie, *Ber.*, 1929, **62**, [*B*], 288; *A.*, 1929, 317.

[29] A. McKenzie and A. K. Mills, *ibid.*, p. 284; *A.*, 1929, 317.

[30] *Idem, ibid.*, p. 1784; *A.*, 1929, 1066.

[31] A. McKenzie, A. K. Mills, and J. R. Myles, *Ber.*, 1930, **63**, [*B*], 904 788.

[32] A. McKenzie and R. Roger, *J.*, 1927, 571; *A.*, 1927, 457.

[33] *Idem, Ber.*, 1929, **62**, [*B*], 272; *A.*, 1929, 317.

[34] A. McKenzie, R. Roger, and G. O. Wills, *J.*, 1926, 779; *A.*, 1926, 610.

[35] M. Tiffeneau and (Mlle.) J. Lévy, *Bull. Soc. chim.*, 1923, [iv], **33**, 759; *A.*, 1923, i, 789.

[36] *Idem, ibid.*, p. 735; *A.*, 1923, i, 788.

[37] *Idem, Compt. rend.*, 1926, **182**, 391; *A.*, 1926, 383.

[38] *Idem, Bull. Soc. chim.*, 1926, [iv], **39**, 763; *A.*, 1926, 818.

regarding the changes. The interpretation of the data is, however, not a simple matter and the complications attending it will therefore be considered in some detail, as sufficient allowance has not always been made for them in the discussion of this subject.

Although essentially similar in character, the rearrangements can be conveniently classified into three main groups : [36] (*a*) the pinacolinic change proper,

$$CRR^1(OH)\cdot C(OH)R^2R^3 \xrightarrow{-H_2O} CRR^1R^2\cdot COR^3$$

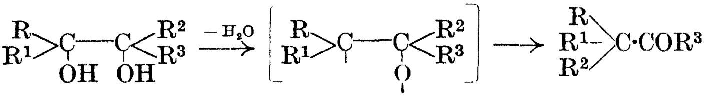
(*b*) the semihydrobenzoinic change in which the tertiary hydroxyl

$$CRR^1(OH)\cdot C(OH)HR^2 \xrightarrow{-H_2O} \begin{cases} CRR^1R^2\cdot CHO \\ \text{or} \\ CHRR^1\cdot COR^2 \end{cases}$$

group is lost, and (*c*) the semipinacolinic change in which the secondary hydroxyl group is lost,

$$CRR^1(OH)\cdot C(OH)HR^2 \xrightarrow{-H_2O} \begin{cases} R\cdot CO\cdot CHR^1R^2 \\ \text{or} \\ R^1\cdot CO\cdot CHRR^2 \end{cases}$$

The pinacolinic change proper presents fewest complications in interpretation. The mode of elimination of the elements of water from the two hydroxyl groups of the pinacol molecule determines which of the two central carbon atoms shall become the ketonic group and thus fixes the general direction of the rearrangement.



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[39] M. Tiffeneau and (Mlle.) J. Lévy, *Compt. rend.*, 1926, **183**, 969; *A.*, 1927, 146.

[40] *Idem, ibid.*, p. 1112; *A.*, 1927, 153.

[41] *Idem, Compt. rend.*, 1927, **184**, 1465; *A.*, 1927, 769.

[42] *Idem, Bull. Soc. chim.*, 1927, [iv], **41**, 1351; *A.*, 1927, 1184.

[43] *Idem, Compt. rend.*, 1928, **186**, 84; *A.*, 1928, 286.

[44] M. Tiffeneau and A. Orékhoff, *ibid.*, 1920, **171**, 400; *A.*, 1920, i, 672.

[45] *Idem, ibid.*, p. 473; *A.*, 1920, i, 673; *Bull. Soc. chim.*, 1921, [iv], **29**, 429, 445; *A.*, 1921, i, 565, 566.

[46] *Idem, Compt. rend.*, 1921, **172**, 387; *A.*, 1921, i, 243; *Bull. Soc. chim.*, 1921, [iv], **29**, 809; *A.*, 1921, i, 788.

[47] A. Orékhoff and M. Tiffeneau, *Bull. Soc. chim.*, 1922, [iv], **31**, 253; *A.*, 1922, i, 458.

[48] M. Tiffeneau and A. Orékhoff, *ibid.*, 1923, [iv], **33**, 195; *A.*, 1923, i, 333.

[49] A. Orékhoff and M. Tiffeneau, *Compt. rend.*, 1924, **178**, 1619; *A.*, 1924, i, 729.

[50] *Idem, Bull. Soc. chim.*, 1925, [iv], **37**, 1410; *A.*, 1926, 172.

[51] *Idem, Compt. rend.*, 1926, **182**, 67; *A.*, 1926, 171.

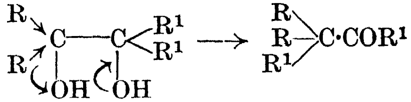
[52] *Idem, Bull. Soc. chim.*, 1927, [iv], **41**, 1174; *A.*, 1927, 1076.

[53] S. Yamaguchi, *Bull. Chem. Soc. Japan*, 1926, **1**, 64; *A.*, 1926, 727.

[54] *Ber.*, 1929, **62**, [*B*], 1598; *A.*, 1929, 929.

[55] E. Luce, *Compt. rend.*, 1925, **180**, 145; *A.*, 1925, i, 263.

In compounds of the type $CRR(OH)\cdot C(OH)R^1R^1$ the nature of the final product is determined by this elimination factor alone and a study of the rearrangements of such compounds completely confirms the view [56] that the elimination of the hydroxyl group occurs preferentially from the carbon atom to which are attached the groups with the greatest capacity for electron release.[57]



$$\begin{matrix}R\\R\end{matrix}\!>\underset{\text{OH}}{\text{C}}\text{—}\underset{\text{OH}}{\text{C}}<\!\begin{matrix}R^1\\R^1\end{matrix} \longrightarrow \begin{matrix}R\\R\\R^1\end{matrix}\!>\text{C}\cdot\text{COR}^1$$

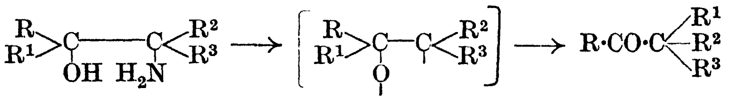
Further support for this view is forthcoming from the data with regard to the less symmetrical pinacols.[e.g., 7, 12, 14, 15, 16, 22, 38, 50] When all the radicals attached to the central carbon atoms are aliphatic the products of the change are usually mixtures involving elimination in both directions.

From the data available it is also possible to arrange certain pairs of groups in the order in which they facilitate the fission of the adjacent hydroxyl group,[13, 14, 19, 26, 33, 37, 46]

$$\text{Alkyl, alkyl} > \text{phenyl, H or } \alpha\text{-naphthyl, H}\left\{\begin{matrix} > \text{benzyl, benzyl} > \text{methyl, H.}\\ > \text{alkyl, benzyl.}\end{matrix}\right.$$

When the substituted ethylene oxides are converted into the isomeric ketonic substances by heating, the fission of the C–O bond follows the same rule,[6, 11, 15, 18, 37, 38] a few apparent exceptions, which occur under drastic conditions,[17] being possibly explicable by a further isomerisation of the primary product.

On the other hand the direction of rearrangement of the αβ-amino-alcohols appears to be determined by the position of the amino-group eliminated, the oxygen of the hydroxyl group remaining in place irrespective of the character of the adjacent groups.[28–32, 34, 39, 55]



$$\begin{matrix}R\\R^1\end{matrix}\!>\underset{\text{OH}}{\text{C}}\text{——}\underset{\text{H}_2\text{N}}{\text{C}}<\!\begin{matrix}R^2\\R^3\end{matrix} \longrightarrow \left[\begin{matrix}R\\R^1\end{matrix}\!>\underset{\text{O}}{\text{C}\text{—}\text{C}}<\!\begin{matrix}R^2\\R^3\end{matrix}\right] \longrightarrow \text{R}\cdot\text{CO}\cdot\text{C}\!\begin{matrix}R^1\\R^2\\R^3\end{matrix}$$

Thus, for example, β-amino-αα-diphenyl-*n*-propyl alcohol (I) is converted by nitrous acid into methyldeoxybenzoin (II),[34] whilst

(I.) $CPh_2(OH)\cdot CHMe\cdot NH_2 \longrightarrow Ph\cdot CO\cdot CHPhMe$ (II.)

in the corresponding pinacol, loss of water occurs by removal of the hydroxyl group from the α-position.[58] Pinacols have, however, been obtained by deamination of some αβ-amino-alcohols,[32] and the possibility of their formation as intermediate products in other cases must not be overlooked.

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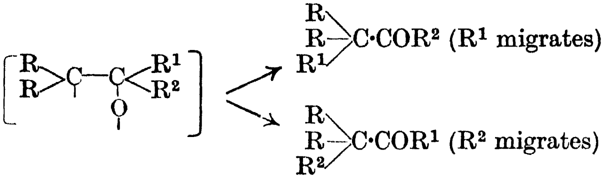
[56] C. K. Ingold, *Ann. Reports*, 1928, **25**, 134.

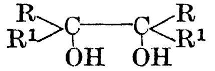
[57] For examples, see list included in Ref. 2 (p. 115).

[58] R. Stoermer, E. Schenck zu Schweinsberg, (Fr.) Sibbern-Sibbers, and P. Riebel, *Ber.*, 1906, **39**, 2288; *A.*, 1906, i, 581.

Although the general direction of a pinacolinic change is determined by the mode of elimination of the elements of water or of fission of the oxide linkage in an ethylene oxide, the nature of the product obtained depends also on the relative facility with which the two groups concerned will migrate from one carbon atom to the other. For example :



The differences in " migratory aptitude " of various groups are best observed in the rearrangement of compounds of type (III) in which

(III.)


$$\begin{matrix}\mathrm{R}\\\mathrm{R}^1\end{matrix}{>}\underset{\mathrm{OH}}{\mathrm{C}}-\underset{\mathrm{OH}}{\mathrm{C}}{<}\begin{matrix}\mathrm{R}\\\mathrm{R}^1\end{matrix}$$

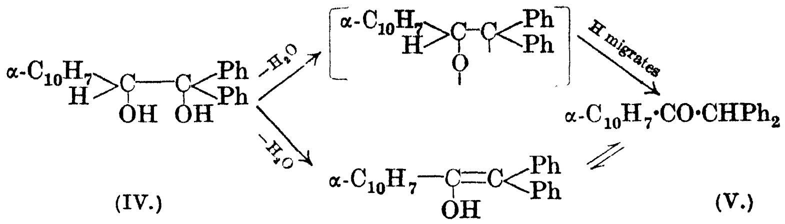
the two hydroxyl groups are identically situated and the elimination factor is therefore not involved. Investigation of the rearrangement of such compounds [1, 2, 10, 60, 61] has shown that the following groups can be arranged in order of decreasing " migratory aptitude " thus :

p-anisyl>*p*-tolyl, *p*-diphenyl,
α-naphthyl>*p*-*iso*propylphenyl>*p*-ethylphenyl> } phenyl
p-fluorophenyl> }
p-iodophenyl { >*p*-bromophenyl, *p*-chlorophenyl>*o*- or *m*-chloro- or -bromo-phenyl
{ >*m*-tolyl>*m*-anisyl

The ease with which these different groups migrate within the molecule is evidently not related simply to any one of their properties and more data will be required before the factors governing " migratory aptitude " in the pinacol–pinacolin system can be fully understood, especially as it has not yet been established that this is a property of the group independent of its environment.

Numerous attempts have been made to deduce the relative " migratory aptitudes " of various groups from observation of the rearrangement of compounds other than type (III), but the interpretation of the results obtained is complicated by the two further considerations discussed below and it is inadvisable to draw from these results any definite conclusions.

When one or more of the four radicals attached to the two central carbon atoms are replaced by hydrogen atoms it is sometimes possible for a given product to be formed in more than one way. For example :



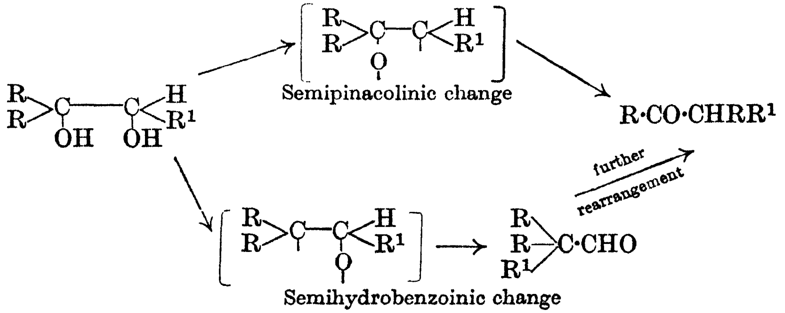
(IV.) (V.)

The transformation of (IV) into (V) by the action of dilute or concentrated sulphuric acid [26] may occur either as a semihydrobenzoinic change with migration of a hydrogen atom or by a vinyl dehydration, followed by ketonisation of the resultant enol. It is not permissible, therefore, to draw any conclusion from this rearrangement as to the relative ease of migration of hydrogen and the α-naphthyl group, and similar caution must be exercised in the interpretation of the numerous other cases of apparent semihydrobenzoinic change which involve the same dilemma.[6, 14, 15, 16, 22, 44, 49, 50, 52]

Yet another complication attends the interpretation of the rearrangement of αβ-glycols having hydrogen atoms attached to the α- or β-carbon atom. It has been shown [3–8, 20, 51, 59] that aldehydes of the type $CR_3{\cdot}CHO$ in the presence of cold concentrated sulphuric acid, or even sometimes on boiling with the dilute acid, may undergo rearrangement into isomeric ketones :

$$CR_3{\cdot}CHO \longrightarrow CHR_2{\cdot}COR.$$

The reagents that are known to bring about the conversion of the aldehydes into the ketones are amongst those most commonly employed to effect the pinacol–pinacolin change, and it is therefore impossible as a rule to decide whether a given ketone, obtained apparently by a direct semipinacolinic rearrangement, is really the primary product.



It is clear, however, that the aldehyde is not necessarily an inter-

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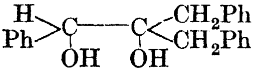
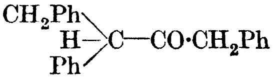
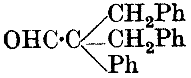
[59] S. Danilov, *J. Russ. Phys. Chem. Soc.*, 1919, **51**, 97.

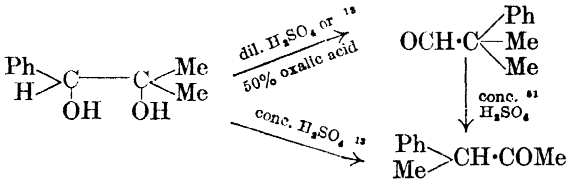
mediate product, as R. Roger and A. McKenzie[33] have shown that the conversion of *d*-β-hydroxy-β-phenyl-αα-dibenzylethanol (VI) into αγ-diphenyl-γ-benzylacetone (VII) by boiling dilute sulphuric acid does not involve complete loss of optical activity as would occur if the ketone were formed by way of the aldehyde (VIII) (compare also A. McKenzie and W. S. Dennler[27] and J. Lévy and P. Weill[20]).


(VI.)


(VII.)


(VIII.)

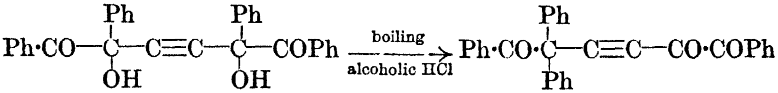
This rearrangement of trisubstituted acetaldehydes affords an explanation of the change in product which often accompanies a change of reagent.[4, 6, 13, 36, 40, 44] For example :



Aldehydes are usually formed under the milder conditions and ketones with the more drastic agents.

The deduction of any series of " migratory aptitudes " from the results of apparent semipinacolinic changes[43] is evidently unsafe unless the mechanism of the rearrangement can be independently demonstrated in each case.

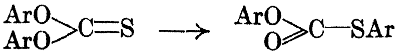
H. Kleinfeller and F. Eckert[54] have described a rearrangement of the pinacol–pinacolin type involving αδ-migration.



$$\mathrm{Ph{\cdot}CO{-}\underset{OH}{\overset{Ph}{C}}{-}C{\equiv}C{-}\underset{OH}{\overset{Ph}{C}}{-}COPh \xrightarrow[\text{alcoholic HCl}]{\text{boiling}} Ph{\cdot}CO{\cdot}\underset{Ph}{\overset{Ph}{C}}{-}C{\equiv}C{-}CO{\cdot}COPh}$$

Other Molecular Rearrangements.

A new triad isomeric change has been discovered by A. Schonberg and L. von Vargha.[62] The diarylthioncarbonates (I) were converted into the corresponding thiolcarbonates (II) when heated at



$$(\mathrm{I.})\quad \mathrm{{ArO \atop ArO}{>}C{=}S \longrightarrow {ArO \atop O}{>}C{-}SAr}\quad (\mathrm{II.})$$

about 300°. The rearrangement has been employed for the prepar-

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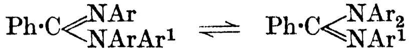
[60] A. Orékhoff and J. Brouty, *Bull. Soc. chim.*, 1930, [iv], **47**, 621; *A.*, 1179.

[61] J. C. Bailar, jun., *J. Amer. Chem. Soc.*, 1930, **52**, 3596; *A.*, 1438.

[62] *Ber.*, 1930, **63**, [*B*], 178; *A.*, 320.

ation from the corresponding phenols of some disulphides otherwise accessible with difficulty.[63]

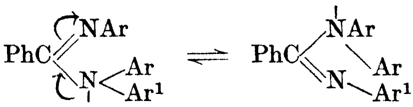
The reversible rearrangement of the triarylbenzenylamidines referred to in last year's Report has now been investigated in greater detail [64] and has been shown to be intramolecular by tests similar to those applied to the imino-ether rearrangement. The relative

(III.)  (IV.)

$$\text{(III.)}\quad \mathrm{Ph{\cdot}C}\left<\begin{matrix}\mathrm{NAr}\\ \mathrm{NArAr^1}\end{matrix}\right. \rightleftharpoons \mathrm{Ph{\cdot}C}\left<\begin{matrix}\mathrm{NAr_2}\\ \mathrm{NAr^1}\end{matrix}\right.\quad \text{(IV.)}$$

mobilities of different migrating groups Ar (III and IV) were in the order p-tolyl<phenyl<p-chlorophenyl, whilst replacement of p-tolyl as the stationary group $\mathrm{Ar^1}$ by p-chlorophenyl resulted in a retardation of interconversion. These results are exactly parallel with those obtained for the rearrangement of imino-aryl ethers into amides [66] and it would appear that the changes are identical in mechanism.

Consideration of the positions of equilibrium of several pairs of isomeric amidines has shown that the original electronic formulation of these rearrangements is untenable, but all the known facts are in agreement with the view [65] that the migrating group Ar first attracts one or both of the lone electrons of the nitrogen atom to which it is going and then, retaining its newly acquired electrons, releases the original binding pair. This view has the advantage, not only of



furnishing a picture of these rearrangements, but also of revealing a close connexion between them and a number of other changes, both intra- and inter-molecular, which at first sight appear quite dissimilar. For instance, an intermolecular reaction of this kind is the displacement of chlorine by iodine in various alkyl chlorides when these are heated with an alkali iodide.[67] The replacement may be regarded as an intermolecular migration of the radical from chlorine to iodine and there is strong evidence that the exchange takes place by a preliminary combination of the alkyl chloride molecule and the iodide ion, followed by ejection of a chlorion. In the same class also come reactions like the fission of diaryl ethers by piperidine,[68] an intermolecular migration of an aryl group from oxygen to nitrogen. Conversely the imino-ether and amidine changes may be regarded as intramolecular displacement reactions.

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[63] A. Schönberg, L. von Vargha, and W. Paul, *Annalen*, 1930, **483**, 107.

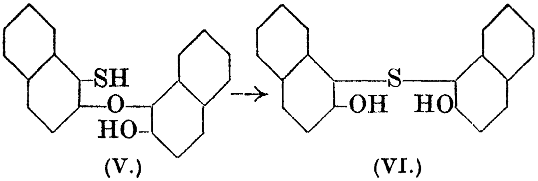
[64] A. W. Chapman, *J.*, 1930, 2458; A. W. Chapman and C. H. Perrott, *ibid.*, p. 2462.

[65] *Ann. Reports*, 1929, **26**, 123.

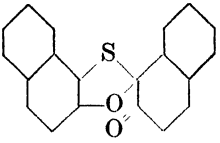
[66] A. W. Chapman, *J.*, 1927, 1743; *A.*, 1927, 874.

[67] Compare *Ann. Reports*, 1929, **26**, 137. [68] *Ibid.*, p. 133.

The establishment of the constitution (V) for *iso*-β-naphthol sulphide [69] reveals the isomeric change of this compound under the influence of heat or alkalis [70] as the migration of a hydroxynaphthyl group from oxygen to sulphur.



(V.) (VI.)



(VII.)

This appears to be an intramolecular change comparable both with the thion–thiol (and imino-ether) rearrangement and with the replacement reactions already discussed. The migration of the β-hydroxynaphthyl radical from oxygen to sulphur is compensated by the reverse migration of the proton. The ortho-quinonoid dehydrosulphide (VII) may be regarded as an oxidised form of the hypothetical intermediate in which both the sulphur and the oxygen atom are momentarily attached to a single nuclear carbon atom.

A more detailed study of the rearrangement of phenacylbenzyldimethylammonium salts mentioned in the last Report has now appeared.[71] For the phenacyl group has been substituted *p*-bromo-

$$[\mathrm{Ph{\cdot}CO{\cdot}CH_2{\cdot}\overset{+}{N}Me_2{\cdot}CH_2Ph}]\overset{-}{\mathrm{O}}\mathrm{H} \longrightarrow \mathrm{Ph{\cdot}CO{\cdot}CH(CH_2Ph){\cdot}NMe_2} + \mathrm{H_2O}$$

phenacyl and acetonyl, for the benzyl group various substituted benzyls, α-phenylethyl, benzhydryl, and 9-fluorenyl, and for the dimethylammonium radical piperidinium without alteration in the character of the rearrangement. The change followed a unimolecular course in alcoholic sodium ethoxide solution and no exchange of radicals could be detected between the molecules of two different compounds undergoing rearrangement in a mixed solution. The relative migration velocities of different substituted benzyl groups were as follows :

Substitutent	*p*-MeO	H	*m*-Br	*p*-Br	*p*-NO_2
Velocity	0·77	1·0	1·6	2·52	about 30

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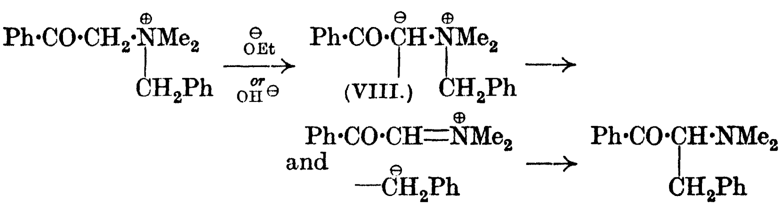
[69] L. A. Warren and S. Smiles, *J.*, 1930, 956; *A.*, 908.

[70] R. Henriques, *Ber.*, 1894, **27**, 3000; *A.*, 1895, i, 103.

[71] T. S. Stevens, *J.*, 1930, 2107; *A.*, 1437; T. S. Stevens, W. W. Snedden, E. T. Stiller, and T. Thomson, *J.*, 1930, 2119; *A.*, 1585; compare *Ann. Reports*, 1929, **26**, 124.

The author's view of the course of the reaction may be represented thus:



$$\underset{\displaystyle\mathrm{CH_2Ph}}{\mathrm{Ph{\cdot}CO{\cdot}CH_2{\cdot}\overset{\oplus}{N}Me_2}} \xrightarrow[\mathrm{or\ OH^{\ominus}}]{\overset{\ominus}{\mathrm{OEt}}} \underset{\mathrm{(VIII.)}\quad\displaystyle\mathrm{CH_2Ph}}{\mathrm{Ph{\cdot}CO{\cdot}\overset{\ominus}{C}H{\cdot}\overset{\oplus}{N}Me_2}} \longrightarrow$$

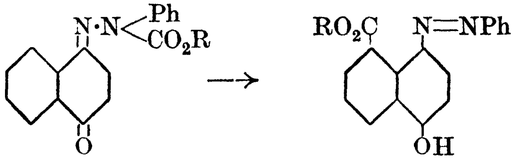
$$\mathrm{Ph{\cdot}CO{\cdot}CH{=}\overset{\oplus}{N}Me_2}\ \text{and}\ \mathrm{-\overset{\ominus}{C}H_2Ph} \longrightarrow \underset{\displaystyle\mathrm{CH_2Ph}}{\mathrm{Ph{\cdot}CO{\cdot}CH{\cdot}NMe_2}}$$

the free benzyl anion being captured again before it can escape into the bulk of the reaction mixture. The facts could be equally well explained along the lines adopted for the cases discussed above. The rearrangement resembles the conversion by heat of *iso*cyanides into nitriles:

$$\mathrm{R{-}N{\equiv}C{-}} \longrightarrow \mathrm{{-}N{\equiv}C{-}R}$$

A remarkable case of the migration of a group from a side chain into the nucleus of an aromatic compound has been recorded.[72] Methyl and ethyl 1 : 4-naphthaquinonephenylhydrazone-*N*-carboxylates (IX), in the presence of cold alcoholic barium hydroxide, yielded, besides the products of hydrolysis, methyl and ethyl 8-benzeneazo-5-hydroxy-1-naphthoates (X), a conversion that

(IX.)



(X.)

involves the migration of the group CO_2R from the β-nitrogen atom in the side chain to the *peri*-position in the naphthalene nucleus.

Phenyl allyl sulphide is partly converted into *o*-allylthiophenol at temperatures above 200°,[73] a rearrangement similar to that of the corresponding oxygen compound.[74]

The difficulties [75] that frequently beset attempts to determine whether a given rearrangement, dependent upon the presence of a catalyst, is or is not intramolecular are again exemplified in a study of the rearrangement of the alkylanilines in the presence of metallic salts.[76] The authors conclude that the change is intramolecular and does not occur by successive fission and recombination of an alkyl halide, but the experimental results can be reconciled with the opposite view. The interesting observation was made that whereas *iso*butylaniline, heated with metallic halides, yielded *p*-amino*iso*butylbenzene, its hydrobromide, heated alone or in the presence of a metallic bromide, underwent rearrangement to *p*-amino-*tert*.-butylbenzene. This was explained as due to a difference in the mechanism of rearrangement in the two cases, but a simpler explanation is that the hydrobromide evolved rapidly a large proportion of *iso*butyl bromide, which isomerised to the tertiary halide in the vapour phase before recombination, whilst the liberation of halide from the mixture of base and salt was so much slower that nuclear substitution occurred before any considerable fraction of the halide had been changed.

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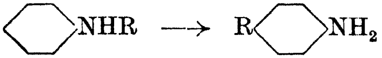
[72] R. Willstätter, E. Ulbrich, L. Pogány, and C. Maimeri, *Annalen*, 1929, **477**, 161; *A.*, 1930, 214.

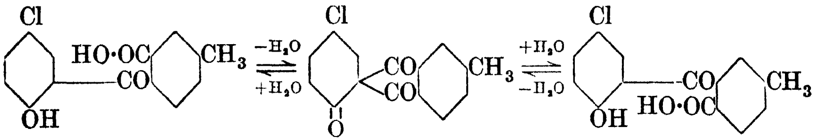
[73] C. D. Hurd and H. Greengard, *J. Amer. Chem. Soc.*, 1930, **52**, 3356; *A.*, 1285.

[74] L. Claisen, *Ber.*, 1912, **45**, 3157; *A.*, 1912, i, 965.

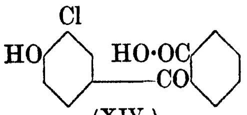
[75] *Ann. Reports*, 1929, **26**, 124.



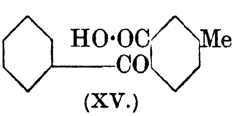
The stereochemical view of the isomerism of the chlorohydroxybenzoyltoluic acids [77] has now been abandoned.[78] The intercovertible pairs are regarded as compounds of the type of (XI) and (XIII), and the rearrangement as proceeding through an intermediate compound (XII) of quinonoid structure. These conclusions are supported by the facts that only one compound could be obtained when phthalic anhydride was substituted for methylphthalic anhydride in the preparation, the two positions for the carboxyl group in (XIV) being equivalent, and that whilst two isomeric compounds, presumably (XV) and (XVI), were obtained by con-



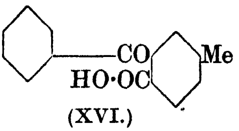
(XI.) (XII.) (XIII.)



(XIV.)



(XV.)



(XVI.)

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[76] W. J. Hickinbottom and (in part) A. C. Waine, *J.*, 1930, 1558; W. J. Hickinbottom and G. H. Preston, *ibid.*, p. 1566; *A.*, 1174.

[77] M. Hayashi, *J.*, 1927, 2516; *A.*, 1927, 1187; *Ann. Reports*, 1929, **26**, 141.

[78] *Idem*, *J.*, 1930, 1513, 1520, 1524; *A.*, 1183.

densation of 4-methylphthalic anhydride with benzene, they were not interconvertible, the essential substituent for the production of quinonoid structure being absent.

Free Radicals

(compare *Ann. Reports*, 1924, **21**, 115; 1928, **25**, 150).

An important event of the last two years has been the demonstration of the real though transitory existence of the free methyl and ethyl radicals.[79] When the vapour of lead tetramethyl was passed at low pressure (1·5—2 mm.) through a heated tube, decomposition occurred and lead was deposited. Passage of the gaseous products of decomposition over a second lead mirror further along the tube caused the disappearance of this mirror with the production of a compound that could be condensed, volatilised, and decomposed by passage through a hot tube to give another deposit of lead. The active material was also capable of attacking metallic zinc and antimony, producing in the former case a substance recognised as zinc methyl. The observed activity fell off rapidly as the distance along the tube increased and disappeared when the material was cooled by means of liquid air. It was therefore concluded that the free methyl radical had been formed by the decomposition of the lead alkyl, and the difficulty of its isolation was accounted for by the very short, though measurable, life period, estimated at 0·006 sec. for half disappearance under the conditions of the experiment. The preparation of the ethyl radical has since been announced. Its compound with zinc has been isolated and found to be convertible into ethyl alcohol and to be free from lead.

Whilst the free methyl and ethyl radicals represent an extreme divergence both in type and in stability from the well-known triarylmethyls, a number of tervalent carbon compounds have been detected which differ to some extent from this class. Such are diphenyl-*tert.*-butylmethyl [80] and diphenylphenylethinylmethyl [81] obtained on warming the corresponding ethanes and detected by the reversible change of colour with change of temperature. The latter is a companion case to that of tetraphenylallyl.[82]

A detailed study of another class of tervalent carbon compound

[79] F. Paneth and W. Hofeditz, *Ber.*, 1929, **62**, [*B*], 1335; *A.*, 1929, 788; F. Paneth and W. Lautsch, *Nature*, 1930, **125**, 564; *A.*, 735. Compare G. Schultze and E. Müller, *Z. physikal. Chem.*, 1930, [*B*], **6**, 267; *A.*, 302; F. Paneth, *ibid.*, **7**, 155; *A.*, 721.

[80] J. B. Conant and N. M. Bigelow, *J. Amer. Chem. Soc.*, 1928, **50**, 2041; *A.*, 1928, 994.

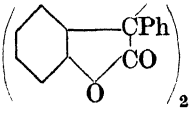
[81] H. Wieland and H. Kloss, *Annalen*, 1929, **470**, 201; *A.*, 1929, 1053.

[82] K. Ziegler, *ibid.*, 1923, **434**, 34; *A.*, 1924, i, 308; *Ann. Reports*, 1928, **25**, 154.

has been carried out by A. Löwenbein and his collaborators [83] on the cyano-, acyl, and lactone derivatives of tetraphenylethane (I to III respectively).

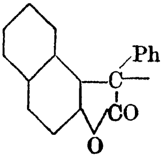
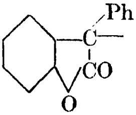
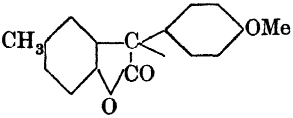
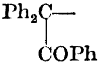
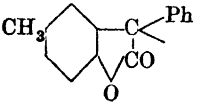
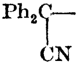
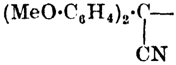
$[CPh_2(CN)—]_2$
(I.)

$[CPh_2(COPh)—]_2$
(II.)



(III.)

These compounds were all colourless and undissociated in the solid state or in cold solution, but became deeply coloured on fusion or when heated in solvents. The dissociation constants were measured by determination of the apparent molecular weights at various dilutions in boiling toluene or ethylene dibromide and the following results were obtained :

	Dissociation constant, in toluene.	Dissociation constant, in $C_2H_4Br_2$.		Dissociation constant, in toluene.	Dissociation constant, in $C_2H_4Br_2$.
	0·0088	0·037		0·00066	0·0043
	0·0016	0·0067	 $\underset{COPh}{Ph_2C—}$	0·00043	—
	0·0011	—	 $\underset{CN}{Ph_2C—}$	dissociation commenced at 140°	
			 $\underset{CN}{(MeO{\cdot}C_6H_4)_2{\cdot}C—}$	dissociation commenced at 60—80°	

Reassociation with corresponding loss of colour occurred when the solutions were cooled. Similar dissociation has been qualitatively observed in the case of benzpinacol dibenzoate in molten naphthalene.[84] The 2 : 3 : 4-trisubstituted dichromenyls [85] also dissociate on solution or fusion, but this case is complicated by the possibility of the free valency occurring on either the 2- or the 4-carbon atom.

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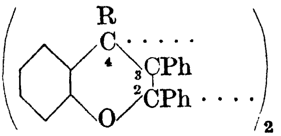
[83] A. Löwenbein and H. Simonis (with H. Lang and W. Jacobus), *Ber.*, 1924, **57**, [*B*], 2040; *A.*, 1925, i, 147; A. Löwenbein (with W. Folberth), *Ber.*, 1925, **58**, [*B*], 601; *A.*, 1925, i, 552; A. Löwenbein and R. F. Gagarin, *ibid.*, p. 2646; *A.*, 1926, 168; A. Löwenbein and H. Schmidt, *Ber.*, 1927, **60**, [*B*], 1851; *A.*, 1927, 1072; A. Löwenbein and L. Schuster, *Annalen*, 1930, **481**, 106; *A.*, 1184.

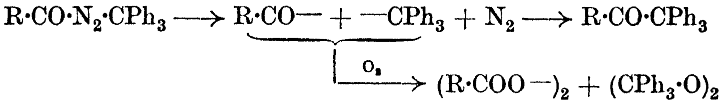
[84] F. F. Blicke, *J. Amer. Chem. Soc.*, 1925, **47**, 1477; *A.*, 1925, i, 811.

[85] A. Löwenbein and B. Rosenbaum, *Annalen*, 1926, **448**, 223; *A.*, 1926, 955.



(R = Ph, α-naphthyl, benzyl.)

The possibility of free radicals being formed as intermediate products in the course of chemical reactions, whilst always admissible, is only occasionally supported by the experimental evidence. Investigations by Wieland and his collaborators [86] of the thermal decomposition of various azo-compounds, however, illustrate this possibility and show that some less well-known types of free radicals are capable of at least momentary existence. When azo-compounds of the type $ArN\colon N\cdot CPh_3$ were heated in inert solvents, nitrogen was rapidly eliminated and triphenylmethyl was recognised among the products. The aryl radical underwent reduction to the corresponding hydrocarbon. Certain aryl compounds $R\cdot CO\cdot N\colon N\cdot CPh_3$ also gave off nitrogen when heated and formed deeply coloured solutions. The colour faded even in the absence of air and the ketone $R\cdot CO\cdot CPh_3$ was obtained from the resulting solution. In the presence of oxygen, however, triphenylmethyl peroxide was formed together, in some cases, with the corresponding acyl peroxide. Evidently the decomposition resulted in the temporary formation of the two free radicals.



$$R\cdot CO\cdot N_2\cdot CPh_3 \longrightarrow \underbrace{R\cdot CO— + —CPh_3}_{} + N_2 \longrightarrow R\cdot CO\cdot CPh_3$$
$$\xrightarrow{O_2} (R\cdot COO—)_2 + (CPh_3\cdot O)_2$$

Determinations of the velocity of dissociation of hexaphenylethane [87] and of various dialkylxanthyls [88] have been made, iodine and oxygen respectively being used to combine with the free radicals as formed. The conclusion of M. Gomberg and F. W. Sullivan [89] that the colour and degree of dissociation of free radicals in solution are not simply related has been criticised for theoretical reasons and on the ground of insufficient accuracy of the experimental evidence.[90]

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[86] H. Wieland, E. Popper, and H. Seefried, *Ber.*, 1922, **55**, [*B*], 1816; *A.*, 1922, i, 772; H. Wieland, H. vom Hove, and K. Börner, *Annalen*, 1925, **446**, 31; *A.*, 1926, 61; H. Wieland, A. Hintermaier, and I. Dennstedt (with J. Lorenzo), *Annalen*, 1927, **452**, 1; *A.*, 1927, 237.

[87] K. Ziegler, L. Ewald, and P. Orth, *Annalen*, 1930, **479**, 277; *A.*, 711.

[88] J. B. Conant and M. W. Evans, *J. Amer. Chem. Soc.*, 1929, **51**, 1925; *A.*, 1929, 934.

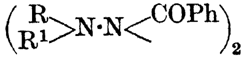
[89] *Ibid.*, 1922, **44**, 1810; *A.*, 1922, i, 929.

[90] C. B. Wooster, *ibid.*, 1929, **51**, 1163; *A.*, 1929, 648.

A further set of optical measurements [91] on solutions of hexaphenylethane, tetraphenyldi-β-naphthylethane, and bis-2 : 3 : 4-triphenyl-6-methylchromenyl in various solvents has shown that, if the ratio $\varepsilon_\nu/\varepsilon_\infty$ of the extinction coefficients at dilution ν and at infinite dilution be taken as a measure of the degree of dissociation of the diradical, Ostwald's dilution law is obeyed. The heat of dissociation of hexaphenylethane calculated from the temperature coefficient of dissociation was found to be about 11·5 kg.-cals. per mol. and to be practically independent of the solvent in which dissociation took place. The kinetics of the oxidation of hexaphenylethane by free oxygen have also been investigated.[92]

In the Annual Report for 1928 it was suggested [93] that the degree of dissociation of substituted hexa-arylethanes was determined largely by the effects of substitution on the stability of the anion Ar_3C and that these effects were not necessarily the converse of those of similar substitution in the kationic radical. The dissociation constants of a number of para-substituted triphenylmethyl chlorides have recently been determined [94] and follow the order $C_6H_4{\cdot}OMe,C_6H_4{\cdot}NO_2,Ph > Ph_3 > C_6H_4{\cdot}OMe,(C_6H_4{\cdot}NO_2)_2 > C_6H_4{\cdot}NO_2,Ph_2 > (C_6H_4{\cdot}NO_2)_2,Ph$, which should be, and is, that of kationic stability. The dissociation of the corresponding hexaphenylethanes could not be studied quantitatively owing to the instability of the compounds, but qualitative observations sufficed to show that the order of radical dissociation was not parallel with the determined order of kationic stability. It is not, however, so easy to reconcile the comparative stability of the undissociated diacyltetraphenylethanes [83] with this suggestion, as the presence of the acyl group should tend to stabilise the anionic radical and so promote dissociation.

On the other hand the stability of free hydrazyl radicals, as was pointed out in the same Report,[93] is not determined by the stability of the anionic form, but is favoured by the simultaneous presence of groups capable of attracting and repelling electrons. A series of 1 : 1 : 4 : 4-tetra-aryl-2 : 3-dibenzoyltetrazanes studied by S. Goldschmidt and J. Bader [95] illustrates still more clearly the validity of this generalisation.



$$\left(\begin{matrix}R\\R^1\end{matrix}\!>\!N{\cdot}N\!<\!\begin{matrix}COPh\\ \end{matrix}\right)_2$$

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[91] K. Ziegler and L. Ewald, *Annalen*, 1929, **473**, 163; *A.*, 1929, 1010.

[92] R. C. Mithoff and G. E. K. Branch, *J. Amer. Chem. Soc.*, 1930, **52**, 255; *A.*, 301.

[93] *Ann. Reports*, 1928, **25**, 154; compare also H. Burton and C. K. Ingold, *Proc. Leeds Phil. Soc.*, 1929, **1**, 421; *A.*, 1929, 1052.

[94] K. Ziegler and W. Mathes, *Annalen*, 1930, **479**, 111; *A.*, 762.

[95] *Ibid.*, 1929, **473**, 137; *A.*, 1929, 1173.

In these compounds a constant electron-restraining influence of considerable magnitude is provided by the benzoyl group on the β-nitrogen atom. The dissociation should therefore be favoured in proportion as the groups R and R^1 have electron-releasing capacities of either inductive or tautomeric kind. This is borne out by the order of the dissociation constants of these compounds, which was found to be (for R and R^1), di-*p*-nitrophenyl<phenyl, *p*-nitrophenyl<di-*p*-bromophenyl<phenyl, *p*-bromophenyl<diphenyl<phenyl, *p*-tolyl<di-*p*-tolyl<phenyl, *p*-anisyl<di-*p*-anisyl. The last compound was completely dissociated in acetone solution.

iso*Cyanides and Related Compounds.*

An important addition to the knowledge of this class of compounds has been made by D. L. Hammick, R. C. A. New, N. V. Sidgwick, and L. E. Sutton,[96] who have obtained conclusive evidence in favour of the formula (I) for the *iso*cyanides in place of the bivalent carbon structure (II) by measurement of the parachors and dipole moments of a number of *iso*nitriles.

$$\text{(I).}\quad \mathrm{R{-}N\overset{\rightarrow}{=}C} \qquad\qquad \mathrm{R{-}N{=}C}\quad \text{(II).}$$

The calculated parachor of the group $\mathrm{{-}N\overset{\rightarrow}{=}C}$ is 62·3, whilst the most probable value for $\mathrm{{-}N{=}C}$ is 40·5. Examination of *p*-tolyl, *p*-anisyl, and ethyl *iso*cyanides gave values of 66, 66, and 69 respectively for the —NC group.

The dipole moment of the group —NC was found from measurements with *p*-tolyl and *p*-chlorophenyl *iso*cyanides to be 3·6 (E.S.U. $\times 10^{-18}$), the carbon being the negative pole. The Nef formula (II) is untenable, since it leads to a value of 2 in the opposite direction, but the experimental result is in good agreement with a computed value for $\mathrm{{-}N\overset{\rightarrow}{=}C}$. The structure thus established is in agreement with the chemical properties of the *iso*nitriles and reveals the identity of the ions (III) derived from both tautomeric forms of hydrogen cyanide. Similar structures can be ascribed to carbon monoxide (IV) [97] and presumably to compounds such as carbon monoxide diethylacetal.[98]

$$\text{(III.)}\quad [\mathrm{{-}N{\equiv}C{-}}]^- \qquad\qquad [\mathrm{{-}C{\equiv}O{-}}]\quad \text{(IV.)}$$

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[96] *J.*, 1930, 1876; *A.*, 1239.

[97] S. Sugden, " The Parachor and Valency," 1930, 171.

[98] H. Scheibler, *Ber.*, 1926, **59**, [*B*], 1022; 1927, **60**, [*B*], 554; *A.*, 1926, 711; 1927, 338; H. Scheibler and E. Baumann, *Ber.*, 1929, **62**, [*B*], 2057; *A.*, 1929, 1296.

Aromatic Substitution

(continued from *Ann. Reports*, 1928, 25, 137).

The two years now under review have seen the publication of much systematic work on the substitution of aromatic compounds, particularly in the diphenyl and other polynuclear series. Several other investigations are worthy of special note, including those dealing with the nitration of phenylboric acid; the directive influence of the nitroso-group; and the manner in which stereochemical factors may control the direction of substitution.

General Theory.—A new orientation rule has been proposed which is at the same time simple and based on the fundamental classification of the elements.[99] It states that, if in a benzene derivative Ph·X·Y, Y is in a higher group of the periodic table than X, or if, being in the same group, Y is of lower atomic weight than X, the group XY is meta-directive, whilst in other cases [including those in which (*a*) X = Y and (*b*) Y is absent] the direction is of the ortho-para type. It must also be borne in mind that ionic charges on XY of positive or negative sign will cause meta- or ortho-para-direction respectively.

Nitrosobenzene seemed to be the only exception to this rule, as bromination of the substance takes place in the para-position in carbon disulphide at − 5°.[1] However, experiment shows that the nitroso-compound is considerably associated under these conditions, and that in acetic acid, in which it is not associated and with which it does not combine, reaction is very slow and no para-substitution can be detected. That the nitroso-group belongs to the meta-directive category is, moreover, clear from the observation that *o*- and *p*-bromonitrosobenzenes react with silver nitrate in glacial acetic acid to yield silver bromide, whereas the *m*-isomeride is unaffected.

A calculation of the net charge on the substituent atom of various groups, assuming the electrons to be shared in the ratio of the nuclear charges of the atoms they unite,[2] places the various substituents approximately in the order of their directing powers. There are, however, some marked divergences, such as the position of the free poles $\overset{\oplus}{N}H_3$ and $\overset{\oplus}{N}R_3$, which should be found at the extreme of *m*-directing groups.

The angle between the plane of a double bond and the adjacent single bonds is according to the tetrahedral theory of the order 125°.

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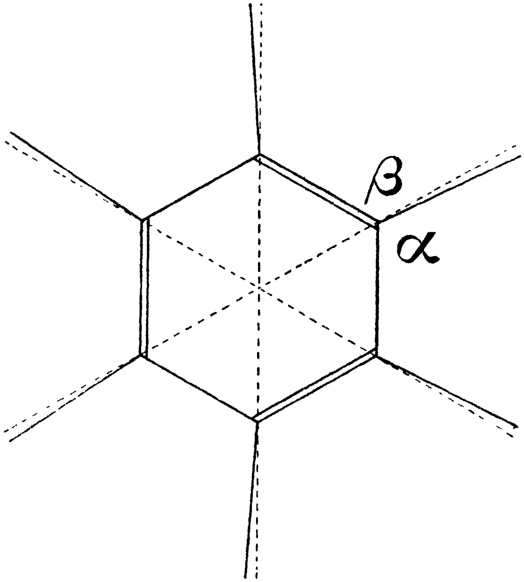
[99] D. L. Hammick and W. S. Illingworth, *J.*, 1930, 2358; *A.*, 1566.

[1] C. K. Ingold, *J.*, 1925, 513; *A.*, 1925, i, 646.

[2] W. M. Latimer and C. W. Porter, *J. Amer. Chem. Soc.*, 1930, 52, 206; *A.*, 331.

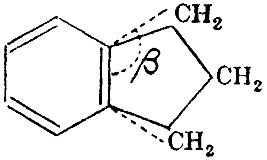
The external valencies of a benzene nucleus of the Kekulé formula should therefore not be directed as from the centre of the hexagon, but should diverge at both sides of each double bond so that the external angle β exceeds the adjacent angle α by an amount which owing to the closure of the ring will be even more than in open-chain olefins (I).[3] Consequently it may be concluded that of the two possible forms of hydrindene (II) and (III), (III) should be the less strained and should constitute the major constituent of the equilibrium mixture of forms.

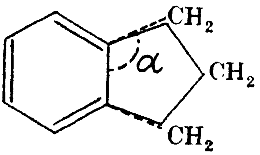
(I.)



In confirmation of this it is found that 5-hydroxyhydrindene is substituted by bromine and by diazonium salts in position 6 rather than 4 : for the analogy between phenols and enols in such reactions makes it reasonable to expect that substitution occurs at the carbon atom joined to the C·OH by means of a double bond, so that the attack on the two possible forms of 5-hydroxyhydrindene (IV and

(II.)





(III.)

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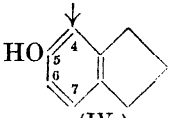
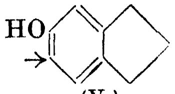
[3] W. H. Mills and I. G. Nixon, *J.*, 1930, 2510.

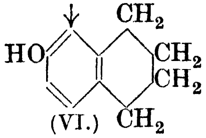
V) would be as indicated by the arrows :[4] structure (V) is therefore



(IV.)



(V.)



(VI.)

indicated for the hydroxyhydrindene and (III) for the parent hydrocarbon. In the same way 5-acetamidohydrindene is brominated in position 6.[5]

On the other hand, *ar*-tetrahydro-β-naphthol is known to be attacked as shown in (VI) and the corresponding acetamidotetrahydronaphthalene reacts in the same (α-) position.[6] Of the two possible structures, formula (VI) consequently represents the arrangement of bonds in the tetrahydronaphthalene nucleus. It is shown by a careful consideration of both the angles and the interatomic distances (different for the aromatic and the alicyclic atoms) that the saturated part of the system would most probably attain a greater freedom from strain by departure from the single plane in this structure (VI) than would be the case for the alternative form in which the common bond between the two rings is a single one.

These arguments reveal important factors which must not be lost sight of in the orientation problem, and they also constitute a remarkable tribute to the value of Kekulé's formula for benzene.

The importance of nitrous acid in certain nitrations has recently been emphasised.[7] As a result of a detailed study of the nitrosation and nitration of phenols, S. Veibel[8] considers that the nitrophenols result from the oxidation by nitric acid of intermediate addition-compounds of phenol and nitrous acid, which are also the precursors of *o*- and *p*-nitrosophenols. Reaction velocity data and the *o*/*p* ratios in nitration and nitrosation are accounted for if the postulated addition compounds are equally readily oxidised but the dehydration to *p*-nitrosophenol is faster than that to the *o*-isomeride.

The directive effects of a series of groups have been determined in recent years by F. Challenger and his associates. The results of the nitration of a number of aromatic thiocyanates and selenocyanates[9] show that the SCN and SeCN groups have far greater *op*-directive powers than the halogens but less than the NHAc group. An interesting point in connexion with the nitration of *o*- and *p*-tolyl thiocyanates is discussed below (see *o*/*p* Ratio, p. 138).

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[4] Compare the coupling of diazonium salts with β-naphthol.

[5] W. Borsche and A. Bodenstein, *Ber.*, 1926, **59**, [*B*], 1910; *A.*, 1926, 1133.

[6] G. Shroeter, *Annalen*, 1922, **426**, 83; C. Smith, *J.*, 1904, **85**, 730; *A.*, 1922, i, 126.

[7] L. A. Pinck, *J. Amer. Chem. Soc.*, 1927, **49**, 2536; F. H. Cohen, *Proc. K. Akad. Wetensch. Amsterdam*, 1928, **31**, 692; M. Battegay, *Bull. Soc. chim.*, 1928, [iv], **43**, 109; H. H. Hodgson and A. Kershaw, *J.*, 1930, 277; *A.*, 1927, 1177; 1928, 272, 402; 1930, 466.

[8] *Ber.*, 1930, **63**, [*B*], 1577, 2074; *Z. physikal. Chem.*, 1930, [*B*], **10**, 22; *A.*, 1033, 1429, 1573.

Another result of importance is the production of 72% of the *m*-substitution product in the nitration of phenylboric acid, $Ph\cdot B(OH)_2$,[10] at − 20°. The boron atom has in this compound only six electrons in the outer shell. Conjugation with the nucleus (+*T* effect) is impossible and the tendency is conversely to attract electrons from the nucleus in order to complete the octet. Consequently *m*-direction prevails. Tribenzylphosphine oxide and dibenzylphosphinic acid are nitrated almost entirely in the *p*-position.

A study of the nitration of a long series of alkyl benzoates gave the following proportions of *m*-nitration product :[11]

Alkyl	Methyl	Ethyl	Propyl	Butyl	Amyl	Hexyl	Heptyl	Octyl
% *m*.........	72·6	69·9	71·8	67·9	68·3	63·7	62·8	60·2

Alkyl	Cetyl	Chloromethyl	β-Chloroethyl	γ-Chloropropyl
% *m*.........	*ca.* 52	81·9	75·8	77·3

Alkyl	β-Bromoethyl	γ-Bromopropyl	*iso*Butyl	*sec.*-Butyl
% *m*.........	71·5	72·8	69·4	65·2

Alkyl	*iso*Propyl	*sec.*-Octyl	*tert.*-Butyl
% *m*.........	64·1	59·4	59·4

The progressive depression of the *m*-directing power of the ester group as the normal carbon chain increases is clearly seen, but there is a definite alternation in the first three and possibly the first five of the series. The effects of branched chains and halogen substitution are fully in accord with the known inductive effects.

The surprising tendency for certain alkyl groups to enter the *m*-position in toluene during its condensation with alkyl halides in presence of aluminium chloride has been confirmed by J. B. Shoesmith and J. F. McGechen.[12] From *tert.*-butyl chloride in presence of either aluminium or ferric chloride, *tert.*-butyltoluene resulted in the ratio *m* : *p* = 65—70 : 35—30. With *n*-butyl chloride the *sec.*-butyltoluenes were obtained, *m* : *p* = 75 : 25.

Positive Poles.—The *m*-orienting influence of oxonium oxygen and quinolinium nitrogen has been observed by R. J. W. Le Fèvre[13] with the 2-phenylbenzopyrylium and 2-phenylquinolinium salts (I) and (II), nitration of which attacks exclusively the positions indicated. No isomerides were detected and the yields were 86% and 100% respectively. 2-Phenylquinoline itself gave 66% of the corresponding nitro-compound.

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[9] F. Challenger and A. D. Collins, *J.*, 1924, **125**, 1377; F. Challenger and A. T. Peters, *J.*, 1928, 1364; F. Challenger, (Miss) C. Higginbottom, and A. Huntingdon, *J.*, 1930, 26; *A.*, 1924, i, 953; 1928, 750; 1930, 332; compare *Ann. Reports*, 1924, **21**, 110.

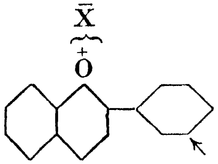
[10] A. D. Ainley and F. Challenger, *J.*, 1930, 2171; *A.*, 1457.

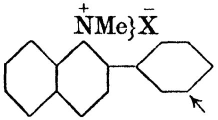
[11] A. Zaki, *J.*, 1928, 983; 1930, 2269; *A.*, 1928, 636; 1930, 1578.

[12] *J.*, 1930, 2231.

[13] *J.*, 1929, 2771; R. J. W. Le Fèvre and F. C. Mathur, *J.*, 1930, 2236; *A.*, 271, 1595.

(I.)





(II.)

The effects of the sulphonium and selenonium groups in aromatic substitution have been determined. A. Pollard and R. Robinson[14] find that benzyldiethylsulphonium picrate yields on nitration 28% of the *m*- and about 61% of the *p*-isomeride. These figures should be compared with those for benzyltriethylammonium picrate (85% *m*)[15] and benzyldiethylamine sulphate (44—52% *m*;[16] 61% *m*).[17] A direct comparison of phenyl and benzyl sulphonium and selenonium salts in nitration has been made by J. W. Baker and W. G. Moffitt,[18] the percentages of *m*-products being :

$\mathrm{Ph{\cdot}\overset{+}{S}Me_2}$	100	$\mathrm{Ph{\cdot}CH_2{\cdot}\overset{+}{S}Me_2}$	52
$\mathrm{Ph{\cdot}\overset{+}{Se}Me_2}$	100	$\mathrm{Ph{\cdot}CH_2{\cdot}\overset{+}{Se}Me_2}$	16

These and previous results all show that for similar compounds the proportion of meta-substitution (*a*) *decreases* with increasing atomic number of the directing atoms in a single *group* of the periodic system, (*b*) *increases* with increasing atomic number in any one *period*. Thus for *m*-directive power we have the series $\overset{+}{N}<\overset{+}{O}$ and $\overset{+}{S}>\overset{+}{Se}$, whereas for *op*-direction we have $N>O>F$.[19]

The fact that a basic group loses its predominant position in the control of substitution when it is converted into a salt, as a result of the relative slowness of the reaction in presence of the positive pole, is illustrated by several recently recorded instances. Thus nitration of *o*- and *m*-bromoanilines in concentrated sulphuric acid[20] takes place in positions 5 and 4 respectively, as shown in (III) and (IV), the bromine atom having the greater influence. Further

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[14] *J.*, 1930, 1765; *A.*, 1302.

[15] F. R. Goss, C. K. Ingold, and I. S. Wilson, *J.*, 1926, 2440; *A.*, 1926, 1132.

[16] B. Flürscheim and E. L. Holmes, *ibid.*, p. 1562; *A.*, 1926, 830.

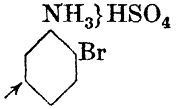
[17] Baker and Ingold, Ref. 27 (p. 136).

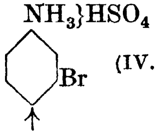
[18] *J.*, 1930, 1722; *A.*, 1302.

[19] *Ann. Reports*, 1926, **23**, 138.

[20] R. Lukeš and J. Fragner, *J. Czech. Chem. Comm.*, 1929, **1**, 294; *A.*, 1929, 804.

(III.)





(IV.)

observations of the nitration of phenylbenzylamine derivatives [21] are fully in accord with modern views. When phenylbenzyl-*n*-butylamine and phenyldibenzylamine are nitrated in sulphuric acid, the isolated products (c. 50% and 21% respectively) are phenyl-*m*-nitrobenzyl-*n*-butylaniline and phenyldi-*m*-nitrobenzylamine. On the other hand, phenyldibenzylamine nitrated in acetic acid, and phenylbenzylnitrosoamine with ordinary nitric acid, are substituted according to the *op* law in the phenyl nucleus as would be expected.[22]

ψ-Acids and ψ-Bases.—It has been pointed out [23] that the anion of a *ψ*-acid such as phenylnitromethane, in which the negative charge may be regarded as distributing itself between the possible tautomeric positions, should undergo *op*-substitution: $\mathrm{Ph{\cdot}CR{:}}\overset{\ominus}{\overparen{\overset{+}{\mathrm{N}}\overset{-}{\mathrm{O}}{\cdot}\mathrm{O}}}$. J. W. Baker has made a study of the nitration of such *ψ*-acids under various conditions.[24] There was considerable meta-substitution in all cases, but the results fully bear out the author's view, the alkali salts showing a much lower proportion of *m*-direction, unless nitric acid of density 1·529 was used. Thus the free phenylnitromethane yielded 67% *m*- + 33% *op*-, but the potassium salt (with nitric acid of density 1·497) gave 42% *m*- + 58% *op*. The contrast was even more striking in the case of ethyl α-nitrophenylacetate, $NO_2{\cdot}CHPh{\cdot}CO_2Et$. These results emphasise the large differences which may arise from small differences in the composition of the nitrating acid, a point shown even more clearly in another paper from the same source describing the nitration of phenylbromocyanonitromethane,[25] where a similar variation in the concentration of the nitric acid raised the proportion of *m*-products from 32% to 94%.

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[21] J. Reilly, P. J. Drumm, and T. V. Creedon, *J.*, 1929, 641; *Sci. Proc. Roy. Dublin Soc.*, 1930, **19**, 377; *A.*, 1929, 691; 1930, 904. Compare *Ann. Reports*, 1928, **25**, 138.

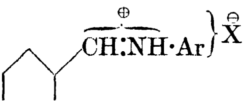
[22] R. D. Desai, *J. Indian Chem. Soc.*, 1928, **5**, 425; *A.*, 1928, 1237.

[23] *Ann. Reports*, 1927, **24**, 115; 1928, **25**, 140.

[24] *J.*, 1929, 2257; *A.*, 1929, 1447; compare B. Flürscheim and E. L. Holmes, *J.*, 1928, 453; *A.*, 1928, 403.

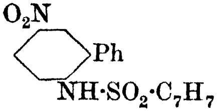
[25] J. W. Baker and C. K. Ingold, *J.*, 1929, 423; *A.*, 1929, 546. See also *Ann. Reports*, 1929, **26**, 124.

Just as ψ-acids with phenyl attached to the ψ-atom show *op*-direction, so ψ-bases tend to direct *m*. B. Flürscheim and E. L. Holmes [26] obtained 87·5% of *m*-nitro-derivative from benzylidene-*m*-nitroaniline, $C_6H_5\cdot CH{:}N\cdot C_6H_4\cdot NO_2$, by nitration in concentrated sulphuric acid. They held that this represented a nitration of the free base, and the result was important, for Flürscheim's theory requires that Ph·CH:NR shall show higher *m*-direction than Ph·CH:O (81% *m*-), whereas the electronic theory leads to the opposite prediction for nitration of the *free base*. Clear evidence has been produced, however, by J. W. Baker and C. K. Ingold [27] that the Schiff's base is present in the sulphuric acid as a salt (V), which was actually isolated. The proportion of *m*-nitro-derivative was moreover reduced by addition of ammonium sulphate from 89% to 84%, the magnitude of which effect is in accordance with expectation, since the salt of which the dissociation is being depressed is a ψ-salt with a neutral form into which it can pass. The situation is therefore reversed and the question may be regarded as decided in favour of the electronic theory.



(V.)

An observation of considerable interest both from a theoretical and a practical point of view is that the *p*-toluenesulphonamido-group has a markedly stronger *op*-directing power than the acetamido-group.[28] For example, 2-*p*-toluenesulphonamidodiphenyl is readily nitrated first in the 5- and then in the 3-position, yielding (I) and (II), whereas 2-acetamidodiphenyl is nitrated in position 4′ to give (III).[29]



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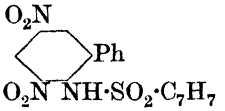

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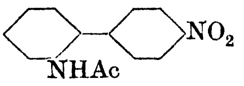
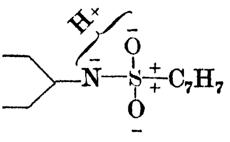


(III.)

The corresponding methylated acyl derivative, 2-*p*-toluenesulphonmethylamidodiphenyl, is nitrated with much greater difficulty at position 5. Bearing in mind the solubility of the unmethylated sulphonamido-compound in alkali, it appears that the nitrogen atom in it has a special directive power owing to a partial negative charge on it, the system being a ψ-acidic one. This is of course suppressed by methylation.



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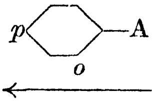
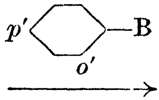
[26] *J.*, 1928, 2230; *A.*, 1928, 1126. [27] *J.*, 1930, 431; *A.*, 594.

[28] F. Bell, *J.*, 1928, 2770; 1929, 2784, 2787; *A.*, 1928, 1367; 1929, 204.

[29] H. A. Scarborough and W. A. Waters, *J.*, 1927, 89; *A.*, 1927, 236.

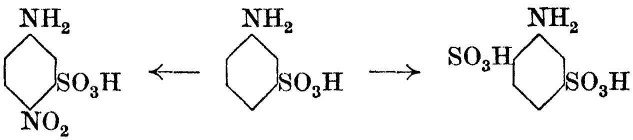
The Ortho-Para Ratio.—In an interesting discussion of the influences which determine the ratio of the ortho- and para-directed products in aromatic substitution, A. Lapworth and R. Robinson[30] conclude that, as a result of the presence in the benzene nucleus of a group A having a smaller attraction for electrons than has the hydrogen atom, electron-availability and therefore reactivity should tend to be greater in the *o*- than in the *p*-position :





With a substituent B which attracts electrons, the potential gradient in the molecular field will be reversed and consequently reaction should occur $p' > o'$. This leads to the expectation of a high *o*/*p* ratio for groups such as Me but a low one for *m*-directive groups such as $\overset{+}{N}R_3$, NO_2 and CO_2H, and also for *op*-directive groups having a natural electron attraction such as Cl, OMe.

The considerable *o*-orientation caused by NO_2, CHO, and $CO{\cdot}CH_3$ is regarded as an anomaly due to the attraction of the reagent to such groups, which are actually known to exert basic functions.[31] The tendency of the nitro-group to enter *o*- to a *m*-directive group has been emphasised by J. Obermiller,[32] who terms this phenomenon " auto-orientation." In this respect there is a sharp contrast between the positions of entry of the NO_2 and SO_3H groups (possibly owing to the greater acidic strength of nitric acid as compared with sulphuric acid). An appreciable proportion of *o*-product is formed in the nitration of nitrobenzene, benzenesulphonic acid, and benzoic acid, but none in the corresponding sulphonations, and the dissimilar products of nitration and sulphonation of metanilic acid also show this effect :



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[30] *Mem. Manchester Phil. Soc.*, 1927, **72**, 43; *A.*, 546; compare *Ann. Reports*, 1926, **23**, 140.

[31] It should be noted to avoid confusion that this view involves a reversal of the explanation given by J. Allan, A. E. Oxford, R. Robinson, and J. C. Smith (*J.*, 1926, 409; *A.*, 1926, 397) where these *o*-substitutions were taken to be normal and the influence of the electrical field was stated in the opposite sense.

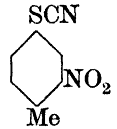
[32] *J. pr. Chem.*, 1914, [ii], **89**, 70; 1930, **126**, 257; *A.*, 1914, i, 513; 1930, 1028.

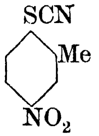
The former authors[30] emphasise the large influence which conditions of reaction may have on the *o*/*p* ratio, and a further disturbing factor which may operate is the steric inhibition of *o*-substitution, nitration of the higher alkylbenzenes being a possible case in point.

Apart from these difficulties this view of the *o*/*p* ratio[33] gives a satisfactory explanation of a large number of facts. Some new cases of this kind will now be referred to.

The contrast between the orientations of the principal products of nitration of *o*- and *p*-tolyl thiocyanates (I) and (II) (compare p. 133), suggesting at first sight that Me has a greater directive power than SCN in one case and a smaller in the other, is clearly a natural consequence of the opposite *o*/*p* ratios which the two groups possess (nitration of toluene, *o* : *p* = 56 : 41 ; of phenyl thiocyanate, *o* : *p* = 20 : 80).

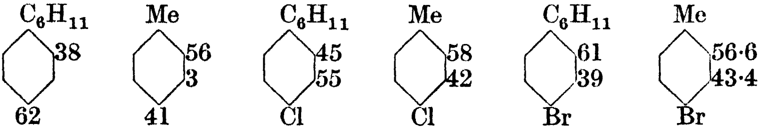
(I.)





(II.)

A study of the nitration of *cyclo*hexylbenzene and its *p*-halogeno-derivatives by H. A. Mayes and E. E. Turner[34] is of interest from the same point of view. The percentages of mononitro-isomerides obtained are indicated by the figures in the following formulæ, data for toluene compounds being added for comparison :



The *cyclo*hexyl group has thus a lower *o*/*p* ratio than methyl in agreement with the behaviour of the higher alkyl groups. The figure of the ratio $p/\frac{1}{2}o$ is 3·3, which may be compared with those for chlorine (4·6) and bromine (3·3). The explanation of the result for *p*-bromo*cyclo*hexylbenzene may lie in a higher level of promotion of reactivity due to alkyl as compared with that due to bromine.

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[33] The interpretation given by C. K. Ingold (*Rec. trav. chim.*, 1929, **48**, 807; *A.*, 1929, 1289; *Ann. Reports*, 1926, **23**, 140) more closely resembles the scheme of J. Allan, A. E. Oxford, R. Robinson, and J. C. Smith, *loc. cit.*

[34] *J.*, 1929, 500; *A.*, 1929, 550, and for comparative data A. F. Holleman and J. P. Wibaut, *Proc. K. Akad. Wetensch. Amsterdam*, 1912, **15**, 594; L. Gindraux, *Helv. Chim. Acta*, 1929, **12**, 921; *A.*, 1913, i, 169; 1929, 1433.

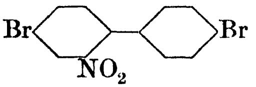
The ratios of *o*/*p*-hydroxy-aldehydes formed in the Reimer–Tiemann reaction from a series of phenols $C_6H_4X{\cdot}OH$ have been found to be as follows : [35]

X	H	*o*-Me	*m*-Me	*o*-Cl	*o*-Br	*o*-I
o/*p*	0·6	0·48	0·46	1·6	1·25	1·07

X	*m*-F	*m*-Cl	*m*-Br	*m*-I	*o*-CO_2H
o/*p*	0·87	0·71	0·72	0·78	0·06

The figures for *m*-Cl, Br, I may be regarded as identical, but they are higher than that for phenol and lower than that for *m*-fluorophenol. These facts are consistent with the directing power of the halogens, which in general promote substitution para with respect to their own position and particularly so in the case of fluorine. The high *o*/*p* value found for *o*-halogenophenols appears to constitute another instance of the tendency for substituents to enter the nucleus in the ortho-position to a strongly *op*-directive group when a second (weaker) *op*-directive atom is next to it (in the *o*′-position), and the relative effect of the halogens (Cl>Br>I) in the present case is in accordance with expectation.[36]

Orientation in Diphenyl Compounds.—Although *pp*′-dibromodiphenyl had been shown to yield on nitration the *o*-nitro-compound (I),[37] *pp*′-difluorodiphenyl was stated [38] to be substituted in the *m*-position to give (II).



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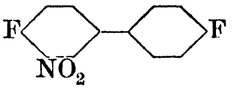

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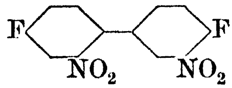

(III.)

R. J. W. Le Fèvre and E. E. Turner find [39] that the latter product does not react with piperidine and must be, not (II), but the fluorine analogue of (I). A second nitro-group enters to give an unsymmetrical product (III), as in the case of the dibromo- and dichlorodiphenyls : one fluorine atom in (III) is removed by piperidine.

Diphenyl and its mono- and di-nitro-derivatives are nitrated in the *o*- and *p*-positions to the extent shown by the figures attached: [40]

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[35] H. H. Hodgson and J. A. Jenkinson, *J.*, 1929, 469, 1639; H. H. Hodgson and J. Nixon, *J.*, 1929, 1632; *A.*, 1929, 559, 1177.

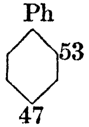
[36] *Ann. Reports*, 1926, **23**, 138; E. L. Holmes, C. K. Ingold, and (Mrs.) E. H. Ingold, *J.*, 1926, 1684; *A.*, 1926, 947.

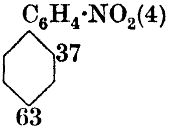
[37] *Ann. Reports*, 1926, **23**, 137.

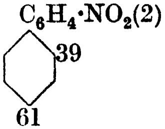
[38] G. Schiemann and W. Roselius, *Ber.*, 1929, **62**, [*B*], 1805; *A.*, 1929, 1052.

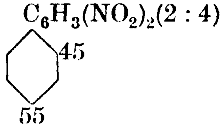
[39] *J.*, 1930, 1158; *A.*, 901.

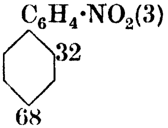
[40] H. C. Gull and E. E. Turner, *J.*, 1929, 491; *A.*, 1929, 547; compare F. Bell, J. Kenyon, and P. H. Robinson, *J.*, 1926, 1239, 2705; *A.*, 1926, 830, 1241; W. Blakey and H. A. Scarborough, *J.*, 1927, 3000; *A.*, 1928, 165.







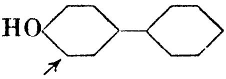


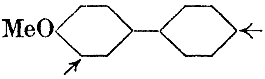


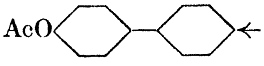
The *o*/*p* ratio is approximately the same in the nitrodiphenyls and is definitely lower than that for diphenyl itself, as it should be. Further nitration gives the 2 : 4 : 4′-trinitro- and the 2 : 4 : 2′ : 4′-tetranitro-compound.

The study of the chemistry of halogeno-, hydroxy-, and amino-diphenyls and their acyl derivatives has engaged the attention of a number of workers, and the resulting orientation data are for the most part normal. Two general conclusions of importance are: that the phenyl or substituted phenyl nucleus exerts a strong *op*-directive effect; and that there is no evidence of conjugation between the nuclei, their behaviour being independent so far as conjugative (tautomeric) effects are concerned.[41] This is in contrast with the behaviour of the phenylpyridines.[42]

The sequence of directing powers $OH > OMe > O{\cdot}SO_2{\cdot}C_7H_7$ is clearly indicated in the results obtained by F. Bell and J. Kenyon [43] in which it is found that 4-hydroxydiphenyl is substituted first in position 3, the methoxy-compound in positions 3 and 4′, and the acyloxy-compound in position 4′ :







There are frequent examples of the well-known tendency for substitution to take place in the second nucleus when a deactivating group is present in the first.[44] Two anomalous cases of substitution were reported,[45] namely, the entry of bromine into the 4′-position in 4-acetamidodiphenyl and of the nitro-group into the 4′-position in 2-acetamidodiphenyl (yield 50%). However, J. Kenyon and

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[41] H. A. Scarborough and W. A. Waters, *J.*, 1926, 557; R. J. W. Le Fèvre and E. E. Turner, *J.*, 1928, 245, 963; *A.*, 1926, 512; 1928, 283, 630.

[42] *Ann. Reports*, 1926, **23**, 136.

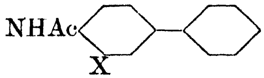
[43] *J.*, 1927, 3044; *A.*, 1928, 145.

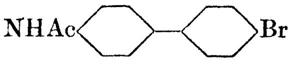
[44] Compare *Ann. Reports*, 1926, **23**, 134; 1928, **25**, 138.

[45] H. A. Scarborough and W. A. Waters, *J.*, 1926, 560; 1927, 89, 1133; *A.*, 1926, 512; 1927, 236, 656.

P. H. Robinson[46] have found that chlorine substitutes the 4-acetamido-compound exclusively in position 3- to give (I) and the reaction with bromine yields the analogous product (I) to the extent of 50% with only 30% of (II). The nitration referred to is not

(I.)

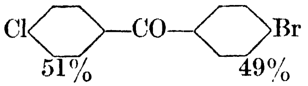


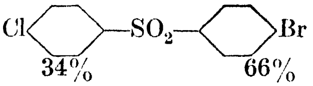


(II.)

surprising, as the sulphuric acid which was present must tend to convert the acetamido-group into a deactivating rather than an activating agent.[47]

Other Polynuclear Types.—The examination of a number of cases of substitution of benzophenones has given straightforward results,[48] but an interesting problem is presented by the proportions of mono-nitration products, as shown by the figures attached to the annexed formulæ, of *pp'*-chlorobromo-benzophenone and -diphenylsulphone :[49]





Nitration of diphenyl ether has given 24% and 44% of *o*- and *p*-nitro-compounds respectively : but in presence of acetic anhydride 46% *o*- and 54% *p*- have been found.[50]

pp'-Dichlorodiphenyl ether is nitrated in the *oo'*-positions (exclusive direction by the oxygen atom), but on the other hand a series of compounds of the type (I), in which A is either an acyl or a nitrated phenyl radical, are nitrated in position 5 as shown, the directive power of the oxygen atom being no doubt reduced by the group A.[51]

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[46] *J.*, 1926, 1242, 3050; *A.*, 1926, 830; 1927, 142.

[47] Compare the nitration of aceto-*p*-toluidide and that of aceto-*m*-4-xylidide; H. E. Dadswell and J. Kenner, *J.*, 1927, 1102; *A.*, 1927, 656. See also Ref. 28 (p. 136).

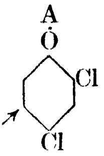
[48] W. Blakey, W. I. Jones, and H. A. Scarborough, *J.*, 1927, 2865; W. Blakey and H. A. Scarborough, *J.*, 1928, 2489; W. A. Waters, *J.*, 1929, 2106; L. Chardonnens, *Helv. Chim. Acta*, 1929, **12**, 649; J. van Alphen, *Rec. trav. chim.*, 1930, **49**, 153, 383; *A.*, 1928, 66, 1246; 1929, 928, 1299; 1930, 476, 603.

[49] L. G. Groves and E. E. Turner, *J.*, 1929, 509; *A.*, 1929, 561.

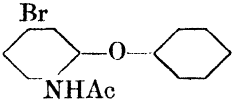
[50] C. M. Suter, *J. Amer. Chem. Soc.*, 1929, **51**, 2581; G. Lock, *Monatsh.*, 1930, **55**, 167; *A.*, 1929, 1174; 1930, 767.

[51] R. J. W. Le Fèvre, S. L. M. Saunders, and E. E. Turner, *J.*, 1927, 1168; L. G. Groves, E. E. Turner, and G. I. Sharp, ~~*J.*, 1929~~, 512; *A.*, 1927, 660; 1929, 551.

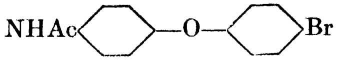
A tendency for substitution in one nucleus of a diphenyl ether to stop when one out of two available *o*-positions in a single nucleus has become occupied has been noticed [52] in certain brominations.



(I.)



(II.)



(III.)

Bromination of *o*- and *p*-acetamidodiphenyl ethers also gives products (II) and (III) in which substitution does not occur *o*- to the acetamido-group. The acetamido-group, it should be remembered, has a low *o*/*p* ratio.

Several other studies of diphenyl ethers have been published.[53]

Some of the earlier work on the nitration of azobenzene was faulty. Nitration or bromination of this substance occurs in positions 4 and 4′, and this result is unaltered by the presence at position 2, 3, or 4 of either Me or Cl. The group $C_6H_5\cdot N{:}N-$ is thus more strongly directive than either chlorine or methyl. On the other hand, methoxyl, amino-, and acetamido-groups supersede the azo-group in controlling substitution in such molecules.[54]

Heterocyclic Compounds.—The nitration of the three isomeric benzylpyridines is of interest in comparison with that of the phenylpyridines [55] previously reported. The amounts of 2-, 3-, and 4-*m*-nitrobenzylpyridines found are 10·4%, trace, and 4·8% respectively. There is thus a reduction of *m*-direction (corresponding amounts of the *m*-nitrophenylpyridines : 2-, 34·9% ; 3-, trace ; 4-, 28·5%), as would be expected from the presence of an extra carbon atom between the pole and the seat of reaction. There is nevertheless a real direction to the *m*-position.

The nitro-group entered chiefly the *p*-position of 2-phenyl-1-methylglyoxaline, 1- and 2-phenylglyoxalines, and 4-phenylpiperidine. The *m*-nitro-compound predominated, however, when 4-hydroxy-2-phenyl-6-methylpyrimidine [56] was nitrated.

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[52] H. A. Scarborough, *J.*, 1929, 2361 ; H. McCombie, W. G. Macmillan, and H. A. Scarborough, *J.*, 1930, 1202 ; *A.*, 1929, 1439 ; 1930, 1034.

[53] (Miss) R. V. Henley and E. E. Turner, *J.*, 1930, 928 ; (Miss) D. L. Fox and E. E. Turner, *ibid.*, pp. 1115, 1853 ; L. C. Raiford and I. J. Wernert, *J. Amer. Chem. Soc.*, 1930, **52**, 1205 ; *A.*, 907, 909, 1283, 767.

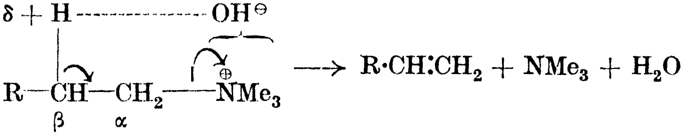
[54] J. Burns, H. McCombie, and H. A. Scarborough, *J.*, 1928, 2928 ; *A.*, 1929, 58.

[55] F. Bryans and F. L. Pyman, *J.*, 1929, 549 ; *A.*, 1929, 577. Compare *Ann. Reports*, 1926, **23**, 136.

[56] R. Forsyth and F. L. Pyman, *J.*, 1930, 397 ; *A.*, 618. Compare *Ann. Reports*, 1924, **21**, 110.

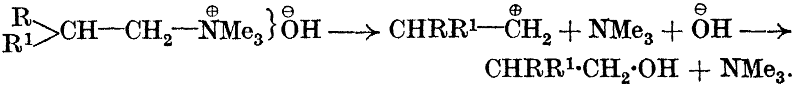
Polar Influences on Properties and Reactions.

Elimination Reactions. Exhaustive Methylation.—In a series of papers on the modes of decomposition of quaternary ammonium and phosphonium compounds and of sulphones, C. K. Ingold and his assistants have elucidated the mechanism of the four reactions which may occur and the structural conditions which determine their relative importance.[57] The first of these (A) is the olefin-elimination familiar in the Hofmann degradation, which takes place according to the scheme :



Wide variations of the structure of the quaternary base affect this reaction in the expected manner. Substitution in the α-CH_2 has little effect and, if complete (absence of α-H), does not prevent reaction A. On the other hand, the character of R hastens or retards it by promoting or suppressing the incipient ionisation of the β-H. Elimination of ethylene (R = H) is thus more ready than that of higher alkylenes (R = alkyl), but styrene (R = Ph) and still more *p*-nitrostyrene are liberated with great ease in accordance with the known repulsion of electrons by alkyl and attraction by phenyl and nitrophenyl.

When reaction A is difficult, the second reaction B occurs, which may be written :



$$\begin{matrix}R\\R^1\end{matrix}\!\!>CH{-}CH_2{-}\overset{\oplus}{N}Me_3\}\overset{\ominus}{O}H \longrightarrow CHRR^1{-}\overset{\oplus}{C}H_2 + NMe_3 + \overset{\ominus}{O}H \longrightarrow$$
$$CHRR^1{\cdot}CH_2{\cdot}OH + NMe_3.$$

This reaction, as the theory requires, becomes increasingly important if R and R^1 contain chains of carbon atoms which branch or extend —the latter effect becoming constant for chains of more than four atoms.

Reaction C, characteristic of phosphonium hydroxides, involves the elimination of a paraffin thus :

$$R_4\overset{\oplus}{P} + \overset{\ominus}{O}H \rightleftharpoons R_4P{\cdot}OH \xrightarrow{\overset{\ominus}{O}H} R_4P\overset{\ominus}{O} \longrightarrow R_3\overset{\oplus}{P}\overset{\ominus}{O} + \overset{\ominus}{R} \xrightarrow{+H_2O} RH + \overset{\ominus}{O}H$$

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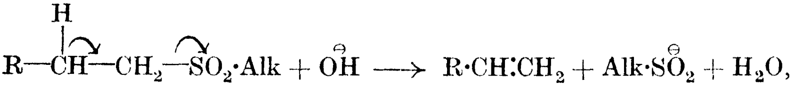
[57] C. K. Ingold with W. Hanhart, *J.*, 1927, 997; C. C. N. Vass, *J.*, 1928, 3125; G. W. Fenton, *J.*, 1928, 3127; 1929, 2338, 2342; 1930, 705; J. A. Jessop, *J.*, 1929, 2357; 1930, 708, 713; *A.*, 1927, 650; 1929, 171, 175, 1423, 1431; 1930, 73, 739, 759. Compare J. v. Braun, W. Teuffert, and K. Weissbach, *Annalen*, 1929, **472**, 121; *A.*, 1929, 1046.

The formation of the undissociated form of the base must involve an increase to ten in the number of electrons in the outer shell of the phosphorus atom. As the nitrogen atom is unable to increase its outer shell, reaction C is impossible with ammonium compounds. The radical R eliminated as paraffin should be that which best tolerates a negative charge, and this is verified by a long series of comparative decompositions. Readiness of elimination is in the order benzyl > phenyl > methyl > β-phenylethyl > ethyl > higher alkyls : carbethoxymethyl is eliminated with great ease.

Reaction C is very facile for phosphonium hydroxides and consequently reaction A is then not normally observed, but by selecting a case where A should be favoured it was found in fact to take place : the hydroxide $\left.CHPh_2\cdot CH_2\cdot\overset{\oplus}{P}Bu_3\right\}\overset{\ominus}{O}H$ gave the olefin $CPh_2{:}CH_2$ and the phosphine as principal products.

Decomposition of sulphones tends to follow a reaction similar to A :



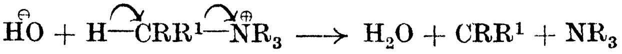
$$R{-}\overset{H}{\overset{|}{C}}H{-}CH_2{-}SO_2\cdot Alk + \overset{\ominus}{O}H \longrightarrow R\cdot CH{:}CH_2 + Alk\cdot\overset{\ominus}{S}O_2 + H_2O,$$

an alkylene and a sulphinate being produced.

Substitution of other negative ions for hydroxyl should affect the extent to which reaction A takes place in any instance. It is found in fact that in the decomposition of the hydroxide, phenoxide, and *m*-nitrophenoxide of a quaternary ammonium salt reaction B is progressively increased at the expense of A, the negative ions involved being in order of diminishing proton-affinity. On the other hand, the ethoxide ion has a greater proton-affinity than hydroxyl. Consequently the sulphone disruption is brought about by sodium ethoxide in many cases where it fails with sodium hydroxide.

Sulphones may also exhibit reaction C, the order in which the radicals tend to this type of elimination being, as the theory requires, the same as for the phosphonium hydroxides.

Finally, a fourth reaction (D) involving 1 : 1-elimination sometimes occurs when β-H atoms are absent :



$$\overset{\ominus}{H}O + H{-}CRR^1{-}\overset{\oplus}{N}R_3 \longrightarrow H_2O + CRR^1 + NR_3$$

The methylene, CRR^1, having only a sextet of electrons, immediately polymerises or isomerises. This has been observed with fluorenyltrialkylammonium hydroxides (which yield bis-*oo*′-diphenylene-ethylene), with the analogous sulphonium hydroxide, and with benzylmethylsulphone. The order of facility of methylenic extrusion (D) is: 9-fluorenyl>benzyl>methyl, which correctly follows the order of anionic stability.[58]

Strengths of Carboxylic Acids.—Dibasic acids. According to the theory of N. Bjerrum [59] the free pole of one carboxyl group of two present in a molecule will affect the active mass of hydrogen ions near the other (about to dissociate), so that the following relation will hold: $\log K_1/K_2 - 0{\cdot}6 = 3{\cdot}1 \times 10^{-8}/r$, where K_1 and K_2 are the first and second dissociation constants of the dibasic acid and r is the distance between the ionic centres.

The subject has been taken up by R. Gane and C. K. Ingold,[60] who from measured values of K_1 and K_2 find the following values of r in Å. for the normal acids $CO_2H{\cdot}[CH_2]_n{\cdot}CO_2H$:

n ..	1	2	3	4	5	6	7
r, Å..........	1·5	5·0	9·2	11·5	13·2	14·5	16·8

Various effects which must tend to influence these figures are discussed. A large distortion of the results must arise from polar effects, of which the chief will be the inductive effect of one carboxyl group on the ionisation of the other—tending to make the apparent value of r too small.

From the third to the seventh acid in the above list the values of r are fairly regular with an average increase of 1·73 Å. per CH_2. The difference between this and the average distance in the crystal (1·26 Å.)[61] is regarded as representing the systematic error due to solvation and electrostriction. The large deviation from the series of values of r shown by the first two members represents the polar effects mentioned and is vanishingly small when three carbon atoms are interposed between the pole and the carboxyl.

This result and those obtained in nitrating the salts

$$Ph{\cdot}[CH_2]_n{\cdot}NMe_3\}X$$ [62]

justify the use of comparative values of r found for β-substituted glutaric acids in connexion with the valency-deflexion hypothesis without fear of error due to the polar effects of the alkyl groups.[63]

A series of determinations with mono- and di-substituted malonic acids, $CRR^1(CO_2H)_2$, gave values of the apparent distances r between the carboxyl groups. The order of these is dissected in a most convincing manner and shown to be not only qualitatively but semi-quantitatively such as should result from the combined operation of the valency-deflexion effect (confirmed in the β-substituted glutaric acids) and the known internal polar effects of the alkyl groups.

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[58] Benzyl>methyl in order of *either* anionic or kationic stability. Compare *Ann. Reports*, 1928, **25**, 121.

[59] *Z. physikal. Chem.*, 1923, **106**, 219; *A.*, 1923, i, 1059.

[60] *J.*, 1928, 1594, 2267; 1929, 1691; *A.*, 1928, 846; 1929, 1144. Compare also A. I. Vogel, *J.*, 1929, 1476; *A.*, 1929, 1009.

[61] W. A. Caspari, *J.*, 1928, 3235; *A.*, 1929, 126.

[62] *Ann. Reports*, 1926, **23**, 131.

[63] This vol., p. 153.

Substituted benzoic acids. The enhanced strength of all *o*-substituted benzoic acids was ascribed by B. Flürscheim [64] to a steric hindrance effect. But a pure steric hindrance, although it might affect the speed of dissociation, should not affect the equilibrium-position. This particular effect of ortho-substituents is better ascribed to a direct polar effect of the substituent on the carboxyl group.[65] The effect of the methyl group in the *o*-position is also to increase the strength of benzoic acid, although its familiar polar effect is to weaken an acid. This indicates the existence of a widely spread electrical field outside the methyl group of an electron-attracting kind : a similarly reversed field must exist outside any polar group at a point on its axis produced into space.[66]

Attention may here be directed to recent determinations of the strengths of the halogenobenzoic acids, the phthalic acids,[67] *p*-cyanobenzoic acid,[68] and α- and β-selenocyanopropionic acids,[69] from which the cyano- and selenocyano-groups are seen to approach the nitro-group in degree of polarity.

Hydrolysis of Esters.—It has for some time been clear that the velocities of hydrolysis and esterification must be influenced by both polar and steric hindrance factors. It was essential to find a method of observing the effects separately or of discriminating between the two effects when superposed. The speeds of alkaline hydrolysis of *m*- and *p*-substituted benzoic esters determined by K. Kindler [70] illustrate the separate polar effect, for steric hindrance due to the substituents must here be negligible. The attack is by hydroxyl and consequently the reaction is facilitated by electron-attracting groups.

An important method for revealing the polar influences in ester hydrolysis independently of steric effects has been developed by C. K. Ingold,[71] starting from the views of H. M. Dawson and of

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[64] *J.*, 1909, **95**, 718; 1910, **97**, 84; *Chem. and Ind.*, 1925, **44**, 246.

[65] A. Lapworth and R. H. F. Manske, *J.*, 1928, 2533; *A.*, 1928, 1245.

[66] G. M. Bennett and A. N. Mosses, *J.*, 1930, 2364; *A.*, 1555.

[67] R. Kuhn and A. Wassermann, *Helv. Chim. Acta*, 1928, **11**, 31, 44; *A.*, 1928, 240.

[68] E. P. Valby and H. J. Lucas, *J. Amer. Chem. Soc.*, 1929, **51**, 2718; *A.*, 1929, 1384.

[69] A. Fredga, *J. pr. Chem.*, 1929, [ii], **121**, 56; *A.*, 1929, 426.

[70] *Annalen*, 1926, **450**, 1; *A.*, 1927, 55. Compare *Ann. Reports*, 1928, **25**, 147, where these results were, owing to an error in abstracting, stated in the inverted order. The speeds of hydrolysis fall in the order of diminishing strengths of the substituted benzoic acids.

[71] *J.*, 1930, 1032, 1375; with (Miss) C. M. Groocock and A. Jackson, *ibid.*, p. 1039; *A.*, 868, 869, 1131.

J. N. Brönsted on reaction catalysis. Whatever may be the detailed mechanism of the reactions,[72] the alkaline hydrolysis depends on the action of hydroxyl and the acid hydrolysis on the action of hydrogen ions. It is demonstrated that the ratio of the velocities of alkaline and acid hydrolysis, k_{OH}/k_H, is probably within wide limits a function of polar factors only (the steric effects cancelling out). Use is made of Dawson's relation : [73]

$$-2p_H^* - \log K_w = \log(k_{OH}/k_H)$$

in which p_H^* is the hydrolytic stability maximum or point of minimum hydrolysis and K_w is the ionic product for water. The progressive polar effects of methyl groups in the hydrolysis of alkyl acetates is shown by the following figures calculated from data available :

Alkyl	Me	CH_2Me	$CHMe_2$	CMe_3
$10^{-2}(k_{OH}/k_H)$	16·1	9·9	4·7	1·5

An extended series of alkyl groups has been studied by using the water-soluble glyceric esters in solutions buffered with sodium glycerate. The order of falling k_{OH}/k_H ratio was Me>Et>Pr>Bu>Am>*iso*-Am>*iso*-Bu>*iso*-Pr, which is clearly in accord with the usual inductive effects of the groups.

In the third memoir the author discusses the various factors controlling the speeds of hydrolysis of esters. The *statistical* factor leads to the expectation that the ratio of the velocities of the first and second stages in the hydrolysis of a symmetrical dicarboxylic ester, k_1/k_2, should be 2·0, and this is true if the ester groups are separated by at least two carbon atoms. Otherwise the *polar* factor is also important. Consideration of the influence of one pole on the reaction at the second carbethoxyl leads for symmetrical dicarboxylic esters to $k_1/k_2 \approx 2\ \exp(7/10^8r)$ and the values of r determined in this way are in general agreement with those found from the dissociation constants.[74] A systematic consideration is also given to steric hindrance and the influence of the medium.

Types of Polar Effect.—It has recently been emphasised by A. Lapworth and R. H. F. Manske [75] that the effect of a substituent on the reactivity of adjacent atoms observed experimentally may result from several superposed influences difficult or impossible to separate. The terms " quantitative " and " electropolar " factors used by B. Flürscheim [76] are advocated ; the former being indicated by the *op*-directive action of a group, and the latter by a comparison of the strengths of the *m*- and *p*-substituted benzoic acids with that of benzoic acid.

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[72] T. M. Lowry, *J.*, 1925, **127**, 1371; J. W. Baker, *J.*, 1928, 1583; *A.*, 1925, i, 886; 1928, 870.

[73] *J.*, 1927, 1146; *A.*, 1927, 632.

[74] This vol., p. 145.

[75] *J.*, 1928, 2533; *A.*, 1928, 1245.

[76] *Loc. cit.*

The increase in availability of electrons at A_1 when $H\text{–}A_1$ is converted by substitution into $A\text{–}A_1$ is termed the "primary internal effect" of A and is written $\underset{\Sigma\text{—}\nearrow}{\overset{\dot{-}}{\mathrm{A}}\text{—}\mathrm{A}_1}$.

Examination of the stabilities of a further series of ketone cyanohydrins shows that the introduction of an alkyl group has (*a*) a stabilising "steric effect" at close quarters and (*b*) a destabilising electropolar influence at points more remote.[77]

The effect of the oxygen atom in $MeO\cdot CH_2Cl$ is to increase the incipient anionisation of the chlorine, which consequently shows high reactivity. In a similar way, although the cyanogen group has a tendency to particularly stable covalent attachment to carbon, the addition of alkali to $HO\cdot CR_2\cdot CN$ produces $\overset{\ominus}{O}\cdot CR_2\cdot CN$ and here the cyanogen becomes rapidly ionised : the aminonitrile $NR_2\cdot CHMe\cdot CN$ is highly unstable. These are cases of an effect related to that of *op*-direction in which the order of efficiency is $\overset{\ominus}{O} > NR_2 > OH$ and OMe.[78]

Both α- and β-chloro-sulphides (and the analogous hydroxy-compounds) are reactive in a similar manner,[79] but the γ-substituted sulphides are entirely unactivated. The effect thus dies out at a distance of the same order as that found in the dicarboxylic acids (p. 145). The δ-hydroxy-sulphide, however, shows a remarkable reactivity which may be attributed to a large activation at moments when the $CH_2\cdot OH$ group is near the sulphur atom in space, an event stereochemically probable.[80]

The possibility should be borne in mind of interpreting the known facts of both aliphatic and aromatic chemistry in terms of two polar effects only : namely, the general polar or electropolar effect (to be regarded as of the nature of both *I* and *D*) and the conjugative or tautomeric effect (*T*).[81] It is at least significant that the effects *D* and *I* have been described as similar "in sign and magnitude in . . . variation as between one directing group and another," [82] and there appears to be no definite evidence that the inductive effect is propagated along saturated carbon chains more than through space. On the other hand the inability of internal polar effects in aliphatic compounds to penetrate beyond the second carbon atom and the parallelism with *op*-directive effects suggest that they are essentially of the tautomeric kind.

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[77] A. Lapworth and R. H. F. Manske, *J.*, 1930, 1976; *A.*, 1251; compare *Ann. Reports*, 1928, **25**, 147.

[78] W. Cocker, A. Lapworth, and A. Walton, *J.*, 1930, 446; *A.*, 571.

[79] G. M. Bennett and A. L. Hock, *J.*, 1927, 477; *A.*, 1927, 355.

[80] G. M. Bennett and A. N. Mosses, *loc. cit.* (Ref. 66; p. 146).

[81] For symbols *I*, *T*, and *D*, see *Ann. Reports*, 1927, **24**, 151; 1928, **25**, 140.

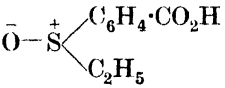
[82] C. K. Ingold, *loc. cit.* (Ref. 33; p. 138).

Stereochemistry.

A valuable general discussion of optical rotatory power has been held during the year.[83] The investigations of W. Kuhn [84] have provided us with a relatively simple theory of the mechanism of the optical activity of dissymmetric molecules, and are of the greatest importance in connexion with the study of rotatory dispersion and of the relation between rotatory power and chemical constitution.

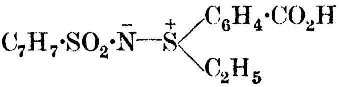
Stereochemistry of Elements of the Sulphur Group (continued from *Ann. Reports*, 1927, 102).—The following results and others described below under "*cis-trans* isomerism of ring compounds" afford abundant evidence in support of the newer view of the steric disposition of the atoms or groups round the sulphur atom in sulphoxides and sulphilimines.

The resolution of the sulphoxide and the sulphilimine derived from *m*-carboxyphenyl ethyl sulphide, namely, the compounds (I) and (II), into their optical antipodes by means of their alkaloidal salts confirms the earlier results.[85] The occurrence of aromatic disulphoxides as pairs of diastereoisomerides has been shown in eight instances, in four of which a single dioxide had been recorded in the literature.[86] Of the two dioxides (III) of 3 : 5-dimethylthiolbenzoic acid, one was found to be resolvable into optically active forms as required by theory whilst the other resisted resolution and is therefore internally compensated.



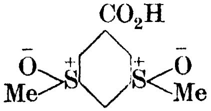
$\overset{-}{O}-\overset{+}{S}<\genfrac{}{}{0pt}{}{C_6H_4\cdot CO_2H}{C_2H_5}$

(I.)



$C_7H_7\cdot SO_2\cdot\overset{-}{N}-\overset{+}{S}<\genfrac{}{}{0pt}{}{C_6H_4\cdot CO_2H}{C_2H_5}$

(II.)



(III.)

An anomaly of long standing has been removed [87] by the re-examination of the mercuri-iodides of optically active sulphonium salts. It is now found that the mercuri-tri-iodide and -tetraiodide,

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[83] *Trans. Faraday Soc.*, 1930, **26**, 266; *A.*, 980.

[84] *Z. physikal. Chem.*, 1929, [*B*], **4**, 14; *Ber.*, 1930, **63**, [*B*], 190; *A.*, 1929, 981; 1930, 276. W. Kuhn and E. Knopf, *Z. physikal. Chem.*, 1930, [*B*], **7**, 292; *A.*, 717.

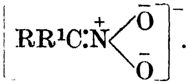
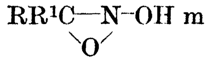
[85] J. Holloway, J. Kenyon, and H. Phillips, *J.*, 1928, 3000; *A.*, 1929, 65.

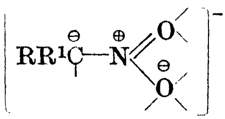
[86] E. V. Bell and G. M. Bennett, *J.*, 1928, 3189; 1930, 1; *A.*, 1929, 179; 1930, 340.

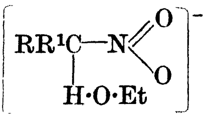
[87] M. P. Balfe, J. Kenyon, and H. Phillips, *J.*, 1930, 2554. Compare W. J. Pope and A. Neville, *J.*, 1902, **81**, 1552.

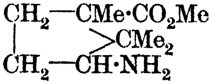
$B[HgI_3]$ and $B_2[HgI_4]$ (where B is phenacylmethylethylsulphonium), and also the cadmi-iodides, $B_2[CdI_4]$ and $B_3[CdI_5]$, are obtainable with considerable rotatory powers but racemise somewhat readily in aqueous solution in presence of iodides.

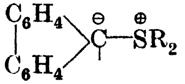
The isolation of enantiomorphous selenonium salts followed rapidly after that of the sulphonium salts, but corresponding evidence in the case of telluronium compounds has hitherto been lacking. The revision last year [88] of our views as to the nature of R. H. Vernon's telluronium di-iodides prepared the way for the announcement [89] of the isolation of phenyl-*p*-tolylmethyltelluronium salts in optically active forms having $[M]_{5461}$ of about 70°. The activity is fugitive, but it indicates that the attached radicals in telluronium compounds are arranged in a similar way to those in sulphonium compounds.

Optically Active aci-*Nitroparaffins and Diazo-compounds. Semi-polar Bond to Carbon.*—The remarkable results of R. Kuhn and H. Albrecht in 1927 have been completely confirmed by an examination [90] of optically active β-nitro-octane. The nitro-compound recovered from the solution of its alkali salt by acidification at − 70° retains more than 70% of its activity. The formula (I) is necessary for the optically active ion, possibly stabilised as a solvate such as (II). The fact that the rotation of the alkaline solution is not affected by keeping for 24 hours seems to exclude the idea that the active ion is in tautomeric equilibrium with the form  $\left[RR^1C{:}\overset{+}{N}\begin{matrix}\diagup\bar{O}\\ \diagdown\bar{O}\end{matrix}\right]^-$. A substance of the structure  $\underset{\diagdown O \diagup}{RR^1C—N}{}^-OH$ may possibly be involved.[91]

(I.) 

 (II.)

(III.) 

 (IV.)

A similar problem is presented by the occurrence of optical activity in aliphatic diazo-compounds. The original formula

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[88] *Ann. Reports*, 1929, **26**, 80.

[89] T. M. Lowry and F. L. Gilbert, *J.*, 1929, 2867; *A.*, 1930, 232.

[90] R. L. Shriner and J. H. Young, *J. Amer. Chem. Soc.*, 1930, **52**, 3332; *A.*, 1269 : compare *Ann. Reports*, 1927, **24**, 103, 107.

[91] G. E. K. Branch and J. Jaxon-Deelman, *J. Amer. Chem. Soc.*, 1927, **49**, 1765; *A.*, 1927, 852.

$R_2C\!<\!\begin{matrix}N\\ \| \\ N\end{matrix}$ for these substances had been largely abandoned in favour of the open-chain formula, which, according to modern views, may be either $R_2C{=}\overset{\oplus}{N}{=}\overset{\ominus}{N}{=}$ or $R_2\underset{|}{\overset{\ominus}{C}}{-}\overset{\oplus}{N}{\equiv}N{-}$;[92] but recent discussion of the physical properties of these substances and the closely related azides has led to the revival of the earlier formula and they are now regarded as partly or wholly cyclic.[93]

On the other hand, the possibility of the occurrence of optically active diazo-compounds was indicated in 1920 and succeeding years,[94] but the observed rotations of the products from which the existence of the active diazo-compounds was inferred were small. The dissymmetry of the carbon atom bearing a diazo-group has now been shown in a more convincing manner by the work of F. E. Ray,[95] who has isolated and compared the modes of decomposition of the diazo-esters from methyl *cis*- and *trans*-aminocamphonanates (III), in the molecule of which there is one asymmetric carbon atom apart from that carrying the amino-group. Decomposition of the *cis*-diazo-compound at low temperatures with dilute acid gave 39·5% of hydroxy-esters and 60·5% of unsaturated esters as compared with 68% and 27% of these products respectively from the *trans*-diazo-compound (of 90% purity). This difference of behaviour points to the existence of diastereoisomeric diazo-compounds and an optically active form $RR^1{-}\underset{|}{\overset{\ominus}{C}}{-}\overset{\oplus}{N}{\equiv}N{-}$ which may perhaps be in tautomeric equilibrium with the cyclic form.

Both the *aci*-nitro-paraffin and the aliphatic diazo-compound thus appear to have in their molecules a semi-polar bond between carbon and nitrogen. The isolation of dimethylsulphonium fluorenylidide [96] (IV) provides a case of such a bond between carbon and sulphur and strengthens the case for the existence of the analogous nitrogen compound. The decomposition of the latter with production of bisdiphenylene-ethylene is similar to the formation of tetraphenylethylene from diphenyldiazomethane.

Ring Formation and Stability.—Reduction of the large ring mono- and di-ketones (*Ann. Reports*, 1928, **25**, 112) by the Clemmensen method has now been described[97] and the resulting *cyclo*paraffins having rings of 12—16 and 22—30 carbon atoms have been examined together with some new diketones as shown in the table of m. p.'s below :

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[92] *Ann. Reports*, 1922, **19**, 85.

[93] *Ann. Reports*, 1929, **26**, 183; H. Lindemann, A. Wolter, and R. Groger, *Ber.*, 1930, **63**, [*B*], 702; *A.*, 586.

[94] C. S. Marvel and W. A. Noyes, *J. Amer. Chem. Soc.*, 1920, **42**, 2259; *A.*, 1921, i, 15; H. M. Chiles and W. A. Noyes, *ibid.*, 1922, **44**, 1798; *A.*, 1922, i, 924; P. A. Levene and L. A. Mikeska, *J. Biol. Chem.*, 1921, **45**, 593; 1922, **52**, 485; *A.*, 1921, i, 233; 1922, i, 818.

[95] *J. Amer. Chem. Soc.*, 1930, **52**, 3004; *A.*, 1281. Compare F. E. Kendall and W. A. Noyes, *ibid.*, 1926, **48**, 2404; *A.*, 1926, 1134.

[96] C. K. Ingold and J. A. Jessop, *J.*, 1929, 2357; 1930, 713; *A.*, 73, 759.

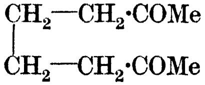
	C_{12}.	C_{13}.	C_{14}.	C_{16}.	C_{18}.	C_{22}.	C_{24}.	C_{26}.	C_{28}.	C_{29}.	C_{30}.	C_{32}.
Hydrocarbons	61°	18°	53°	57°	—	46°	47°	42°	48°	47°	56°	—
Monoketones	—	—	—	—	41°	32	36	42	45	—	—	—
Diketones	—	—	—	—	—	—	65	69	73	—	—	78°

The production of analogous five- and six-membered (heterocyclic) rings by internal sulphonium salt formation from phenyl δ-chlorobutyl and ε-chloroamyl sulphides proceeds as a measurable first-order reaction and at 80° the five-membered ring is produced seventy-six times as fast as the six-membered. This ratio is remarkably close to that (70 : 1) found for the similar ring-closure which occurs in δ- and ε-chloro-amines in presence of alkali.[98] The authors regard this ratio as being a measure of the statistical probabilities of approach within atomic distance of the two ends of the five- or six-atom chain during the course of molecular vibrations without appreciable strain.

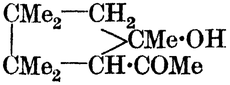
The Valency-deflexion Hypothesis.—A number of further applications of the Thorpe–Ingold hypothesis have been made in recent years, of which one or two will be selected for mention.

The large effect on ring stability caused by the presence of two *gem*-dimethyl groups is well illustrated[99] by the fact that, whereas αδ-diacetylbutane is a normal diketone (V), the corresponding tetramethyl compound reacts exclusively in the cyclic form (VI).

(V.)



$$\begin{array}{l} CH_2\text{—}CH_2\cdot COMe \\ | \\ CH_2\text{—}CH_2\cdot COMe \end{array}$$



$$\begin{array}{l} CMe_2\text{—}CH_2 \\ |\qquad\qquad >CMe\cdot OH \\ CMe_2\text{—}CH\cdot COMe \end{array}$$

(VI.)

A similar progressive influence is evident among the three compounds (I), (II), and (III),[1] the introduction of two successive methyl groups into the open-chain compound (I) converting it first into a ring-chain tautomeric mixture (II) and then into a stable ring compound (III) :

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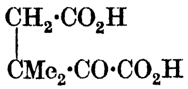
[97] L. Ruzicka, M. Stoll, and others, *Helv. Chim. Acta*, 1930, **13**, 1152; *A.*, 1422.

[98] G. M. Bennett, F. Heathcoat, and A. N. Mosses, *J.*, 1929, 2567; *A.*, 61; H. Freundlich and A. Krestovnikov, *Z. physikal. Chem.*, 1911, **76**, 79; *A.*, 1911, ii, 266.

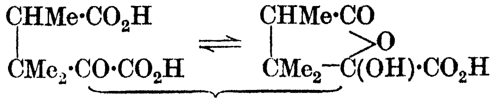
[99] I. Vogel, *J.*, 1927, 594; *A.*, 1927, 449.

[1] E. Rothstein and C. W. Shoppee, *J.*, 1927, 531; *A.*, 1927, 447.



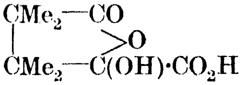
$$\begin{array}{l} CH_2{\cdot}CO_2H \\ | \\ CMe_2{\cdot}CO{\cdot}CO_2H \end{array}$$

(I, stable.)



$$\underbrace{\begin{array}{l} CHMe{\cdot}CO_2H \\ | \\ CMe_2{\cdot}CO{\cdot}CO_2H \end{array} \rightleftharpoons \begin{array}{l} CHMe{\cdot}CO \\ |\qquad\quad >O \\ CMe_2{-}C(OH){\cdot}CO_2H \end{array}}$$

(II, tautomeric mixture.)



$$\begin{array}{l} CMe_2{-}CO \\ |\qquad\quad >O \\ CMe_2{-}C(OH){\cdot}CO_2H \end{array}$$

(III, stable.)

The speeds of alkaline hydrolysis of substituted malonic ester were found by R. Gane and C. K. Ingold [2] to be in the following descending order: *cyclo*propane-1 : 1-dicarboxylic ester>*cyclo*butane-1 : 1-dicarboxylic ester>*gem*-dimethylmalonic ester>*cyclo*hexane-1 : 1-dicarboxylic ester>*gem*-diethylmalonic ester. This order agrees in the main with the series of valency angles 0 computed for groups $R_2C<_{\theta}$ and $C_n>C<_{\theta}$.

Other recent investigations of the valency-deflexion effect have concerned keto-lactol tautomeric mixtures, cyclic anhydrides, imides, and lactones.[3]

The valency-deflexion hypothesis has been criticised by W. Hückel and defended by its authors.[4] There should now be no doubt that the work carried out with its aid has abundantly shown a graduated alteration of the ease of closure and the stability of rings by the presence, in the chain of carbon atoms from which the rings are formed, of a group of the type $R_2C<$ or $C_n>C<$. The computed valency angles do in general agree in respect of their order with the order deduced from experiments, but they cannot, as the authors admit, be regarded as having more than a qualitative significance.

The contention that polar effects should not be admitted to simultaneous consideration is unwarranted, for cases can be selected which demonstrate the valency deflexion and polar effects independently, and their combined effects in more complicated cases have been analysed with remarkable success.[5] In the β-substituted glutaric acids the polar effects of the substituents on the carboxyl groups are in general negligible, and the distances between the two ionising groups calculated from the first and second dissociation constants are in the order: glutaric acid$\gg$β-methylglutaric acid>

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[2] *J.*, 1926, 10; *A.*, 1926, 249.

[3] M. Qudrat-i-Khuda, *J.*, 1929, 1913; 1930, 206; *A.*, 1929, 1273; 1930, 471; E. H. Farmer and J. Kracovski, *J.*, 1927, 680; *A.*, 1927, 447; S. S. G. Sircar, *J.*, 1927, 600, 1252, 1257; 1928, 898; *A.*, 1927, 451, 756; 1928, 618.

[4] *Fortschritte der Chemie, Physik und physikalischen Chemie*, 1927, **19**, 4; *J.*, 1928, 1318; *A.*, 1928, 1173.

[5] This vol., p. 145.

β-*n*-propylglutaric acid > ββ′-dimethylglutaric acid > *cyclo*pentane-1 : 1-diacetic acid > *cyclo*heptane-1 : 1-diacetic acid > *cyclo*hexane-1 : 1-diacetic acid > ββ′-diethyl- and ββ′-dipropyl-glutaric acids.[6] This is not only in general agreement with the valency-deflexion hypothesis, but in detail reproduces minor peculiarities previously discovered by experiments on the closure and stability of rings.

The influence of the *cyclo*hexane ring on the valency angle appears, at first sight, to constitute a serious anomaly. That ring was originally shown to confer added stability on a three-membered ring sharing a spiran carbon atom with it.[7] Such an effect had been expected, for the angle of 120° of a *plane* hexagonal ring should cause the external valency angle to fall to 107¼°. But from our present knowledge of strainless forms of rings of six or more carbon atoms, in which the angles presumably approximate to the tetrahedral value of 109½°, this result evidently needs further consideration.

An experimental discovery of the failure of a large ring to exert the effect originally anticipated was announced for the case of the seven-membered ring by J. W. Baker and C. K. Ingold in 1923 [8] and the suggestion that the ring relieved its strain by becoming non-planar was then made, independently of the announcement of the isolation of the first static isomerides with fused non-planar rings.[9] Yet the influence of the six-carbon ring originally observed has been repeatedly confirmed and the *cyclo*heptane ring has consistently exerted an effect lying between those of the *cyclo*pentane and *cyclo*hexane rings. This may be justified as follows : [10] some strain is necessarily involved in the interconversion of the two possible strainless forms of the *cyclo*hexane ring, and, as isomeric forms have not been isolated, it must be assumed that such an interconversion is continually taking place in the course of molecular agitation and vibration, so that the average effect of the ring is that of a partly strained and not a strainless form. If the *cyclo*heptane ring becomes strained by molecular vibration, this may be of less duration than in the six-membered ring, so that the average strain may be in the order 6-ring > 7-ring > 5-ring. This seems the more credible from a consideration of the fact that movements involving rotation round a bond may be more easy in the *cyclo*heptane ring, so that an almost strainless interconversion of forms should occur.

The valency-deflexion effect of the *trans*-decalin ring has been investigated recently by K. A. N. Rao,[11] who concludes from a study of *trans*-decalin-β-*spirocyclo*propane derivatives that the decalin ring exerts less influence on the valency angle than the free *cyclo*hexane ring. The yield in ring-closure was the same as with *cyclo*hexane and *cyclo*heptane derivatives : the difference is deduced from observations of the disruption of the compounds by acid of various strengths. The facts relating to a series of these spiran compounds and caronic acid are here tabulated for comparison :

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[6] R. Gane and C. K. Ingold, *J.*, 1928, 2267; *A.*, 1928, 1083; compare C. H. Spiers and J. F. Thorpe, *J.*, 1925, **127**, 538; *A.*, 1925, ii, 395.

[7] *Ann. Reports*, 1915, **12**, 109.

[8] *Ibid.*, 1923, **20**, 103.

[9] *Ibid.*, 1924, **21**, 92.

[10] J. W. Baker, *J.*, 1925, **127**, 1680; *A.*, 1925, i, 1277.

Acid.	Mildest conditions for disruption.
Caronic acid	5% HCl at 200°
*cyclo*Pentane*spirocyclo*propanedicarboxylic acid	5% HCl at 200°
Decalin-*β*-*spirocyclo*propanedicarboxylic acid	10% HCl at 240°
*cyclo*Heptane*spirocyclo*propanedicarboxylic acid	20% HCl at 240°
*cyclo*Hexane*spirocyclo*propanedicarboxylic acid	Stable to 20% HCl at 240°

This evidence, as it stands, certainly seems to support the idea that *cyclo*hexane is more strained than decalin, but it is not decisive. The argument is weakened by the fact that only in the case of caronic acid was a definite product of disruption (terebic acid) isolated from these reactions. The fact that *trans*-decalin-2 : 2′-diacetic acid was found to be stable under the conditions of the disruption experiment cannot be held to exclude entirely the possibility that the decalin nucleus of the spiran is broken, for a condition of strain is no doubt imposed upon it by the other rings.

Such experiments would in any case afford very indirect evidence of the valency-deflexion effects, whereas the calculation from the two dissociation constants of the substituted glutaric acids is as direct a confirmation as could be desired.

It may be pointed out, in conclusion, that many chemists will consider it simpler to explain a number of the effects which have been studied under this heading as due to steric hindrance rather than to a secondary consequence of a valency deflexion. This applies particularly to the experiments on the hydrolysis of esters and the disruption of lactone and imide rings, in which the general screening effects of the substituents may be the principal factor.

Stereoisomerism of Ring Compounds.—Parachlorals. The polymerisation of mono- and di-chloroacetaldehydes under the influence of acids yields, in addition to amorphous meta-aldehydes, probably of high molecular weight, crystalline trimeric para-aldehydes to which a six-atom ring structure may be given. From chloral, only polymerides of the meta type were known, but F. D. Chattaway and E. G. Kellett [12] have obtained by the action of cold sulphuric acid a mixture of two crystalline parachlorals. They were separated and are no doubt *cis-* and *trans*-isomerides, (I) and (II), as are the two parabutylchlorals similarly prepared from butyl chloral $CH_3{\cdot}CHCl{\cdot}CCl_2{\cdot}CHO$.

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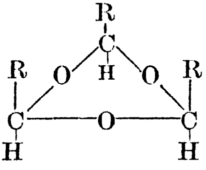
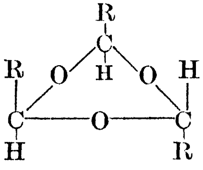
[11] *J.*, 1929, 1954; 1930, 1164; *A.*, 1929, 1297; 1930, 914.

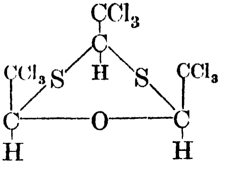
[12] *J.*, 1928, 2709; 1929, 2908; *A.*, 1928, 1357; 1930, 194.



(I.)

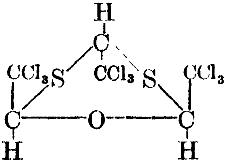


(II.)

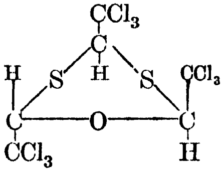


(III.)

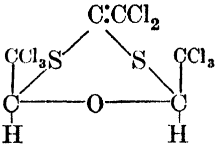
The analogous trichloralimides $(CCl_3{\cdot}CH{:}NH)_3$ have long been known.[13] The action of sulphuric acid on chloralsulphydrate yielded a mixture of trithioparachloral (one of the two possible isomerides) and two dithioparachlorals. Three isomerides are possible (III—V), of which (V) is potentially resolvable. The



(IV.)



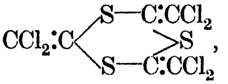
(V.)



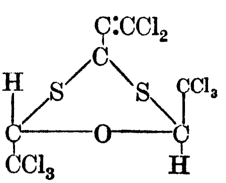
(VI.)

behaviour of these substances gives some information as to their configuration.

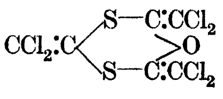
Alcoholic potassium acetate removes the elements of hydrogen chloride from trithioparachloral to give 2 : 4 : 6-trisdichloromethylene-1 : 3 : 5-trithian,



$CCl_2{:}C\left\langle\begin{matrix}S{-}C{:}CCl_2\\S{-}C{:}CCl_2\end{matrix}\right\rangle S$, and the two dithioparachlorals furnish two distinct bistrichloromethylmonodichloromethylene compounds, the trichloromethyl group adjacent to both sulphur atoms being attacked preferentially. The latter products must therefore be (VI) and (VII), from which it is clear that either

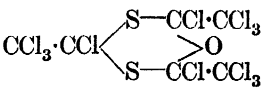


(VII.)



$$CCl_2{:}C\left\langle\begin{matrix}S{-}C{:}CCl_2\\S{-}C{:}CCl_2\end{matrix}\right\rangle O$$

(VIII.)



$$CCl_3{\cdot}CCl\left\langle\begin{matrix}S{-}CCl{\cdot}CCl_3\\S{-}CCl{\cdot}CCl_3\end{matrix}\right\rangle O$$

(IX.)

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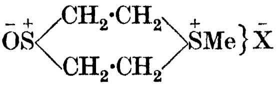
[13] A. Béhal and E. Choay, *Ann. Chim. Phys.*, 1892, **26**, 34; *Compt. rend.*, 1890, **110**, 1270; *A.*, 1890, 1093.

(III) or (IV) must be the missing third isomeride, as these two would yield the same dichloromethylene derivative (VI). One of the two dithioparachlorals isolated is therefore the *dl*-compound (V).

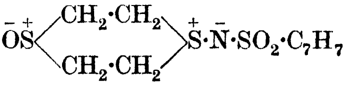
These substances are converted by alcoholic potassium cyanide into the trisdichloromethylene compound (VIII), the isomerism vanishing. Chlorine combines with this compound to produce the trichlorotristrichloromethyl derivative (IX), but once again two isomerides were found in place of the three theoretically possible.

Sulphoxides and related substances. In continuation of the study of the *cis-trans* isomerism arising from the non-planar configuration of the sulphoxide and related groups[14] several further pairs of derivatives of 1 : 4-dithian have been described.[15] Cautious oxidation of dithian yielded a monosulphoxide, from which two isomeric dithian monoxide methylsulphonium salts (I) and two monoxidesulphilimines (II) were prepared. Moreover the bis-sulphilimine of dithian (III)[16] was separated into two distinct isomerides by crystallisation from solvents of high boiling point.



cis and *trans*.

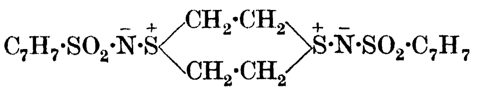
(I.)



cis and *trans*.

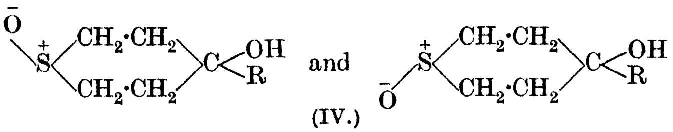
(II.)

(III.)



cis and *trans*.

A closely analogous case is that of the sulphoxides of penthianols, which occur in isomeric pairs of the type (IV).[17]



(IV.)

The oxidation of phenylpenthianol (R = Ph), benzylpenthianol (R = CH_2Ph), and penthianolcarboxylic acid (R = CO_2H) gave in each case two distinct isomerides. The methylsulphonium salt and sulphilimine of phenylpenthianol were also examined : the former was separated into *cis*- and *trans*-forms which are similar in type to the isomeric 4-substituted piperidinium salts;[18] but a second isomeric sulphilimine could not be found.

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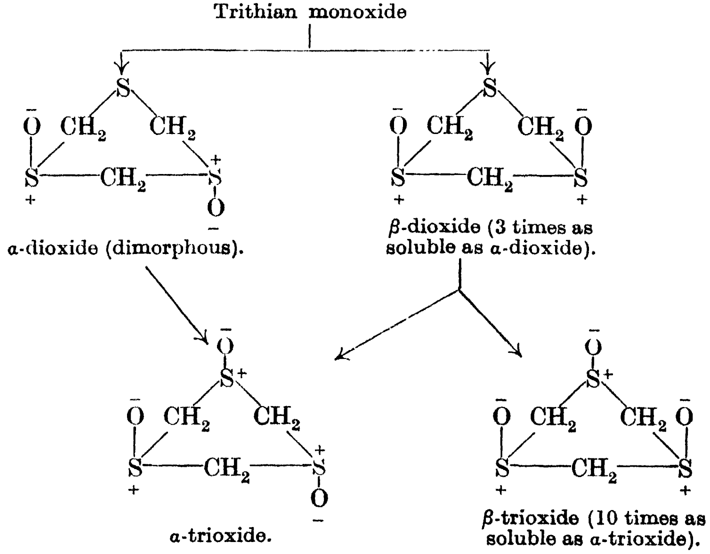
[14] *Ann. Reports*, 1927, **24**, 103.

[15] E. V. Bell and G. M. Bennett, *J.*, 1928, 86; *A.*, 1928, 299.

[16] F. G. Mann and (Sir) W. J. Pope, *J.*, 1922, **121**, 1052.

[17] G. M. Bennett and W. B. Waddington, *J.*, 1929, 2832; *A.*, 219.

Hitherto trimethylene trisulphide (trithian) has been known[19] to give rise to a single dioxide and a single crystalline trioxide (disregarding a further amorphous oxidation product having the characteristics of a substance of high molecular weight). A study of the regulated oxidation of trithian has now not only led to the isolation of all the theoretically possible mono-, di-, and tri-sulphoxides derived from it but also provided convincing evidence as to their configurations.[20] The results are summarised in the annexed scheme of oxidations :


Trithian monoxide
O
CH₂
S
+
α-dioxide (dimorphous).
β-dioxide (3 times as soluble as α-dioxide).
α-trioxide.
β-trioxide (10 times as soluble as α-trioxide).

The compounds previously known were the β-dioxide and the α-trioxide. The configurations of the dioxides are fixed by the fact that one is oxidised to a single trioxide and the other to both trioxides. Moreover the common product of oxidation of both dioxides is necessarily the *trans*-trioxide, and the other trioxide the *cis*-isomeride. The same configurations would have been assigned to these isomerides on the ground of their relative solubilities in water, and this justifies the configurations previously allocated to the dithian dioxides.[21]

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[18] *Ann. Reports*, 1927, **24**, 102.

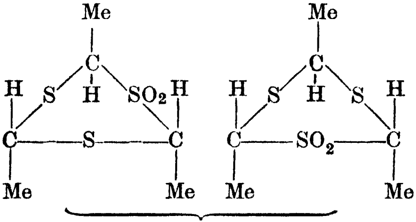
[19] O. Hinsberg, *J. pr. Chem.*, 1912, [ii], **85**, 337; 1913, [ii], **88**, 49; *A.*, 1912, i, 546; 1913, i, 818.

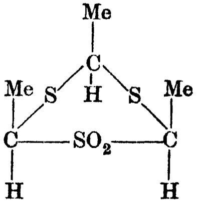
[20] E. V. Bell and G. M. Bennett, *J.*, 1929, 15; *A.*, 1929, 293.

[21] *Ann. Reports*, 1927, **24**, 103.

The view that the supposed third isomeride of trithioacetaldehyde is a mixture of the α- and β-compounds has been confirmed.[22] The oxidation of these trisulphides has been re-examined [23] and, although the numerous possible isomeric sulphoxides were not all isolated, the results supply a definite proof that the configurations allocated to the trithioacetaldehydes (on physical grounds) must be reversed. The results are summarised in the following table :

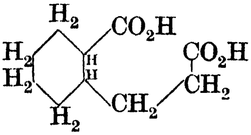
Isomeride.	Configuration.	Oxidation products, expected.	Oxidation products, found.
a-, m. p. 101°	*trans* (hitherto *cis*)	4 Monoxides 2 Monosulphones	2 Monoxides 2 Sulphones
β-, m. p. 126°	*cis* (hitherto *trans*)	2 Monoxides 1 Monosulphone	1 Monoxide 1 Sulphone

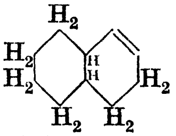

Two *trans*-sulphones.

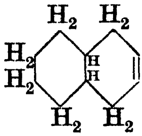

One *cis*-sulphone.

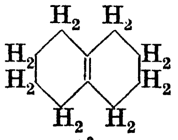
All three possible monosulphones were thus found, and the trithioacetaldehyde which yielded only one of them must have the *cis*-configuration.

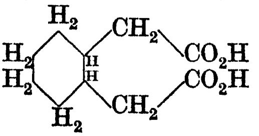
cis-trans-*Fused rings.* (1) *Octahydronaphthalenes.* Five isomeric octahydronaphthalenes should be possible (II—IV). Of these


(I.)


Δ^1 *cis* and *trans*.
(II.)


Δ^2 *cis* and *trans*.
(III.)

(IV.)

Δ^9.


(V.)

hydrocarbons, the *trans*-Δ^2-isomeride was prepared and examined by H. Leroux in 1910 [24] and the *cis*-Δ^2-isomeride by W. Borsche and E. Lange in 1923 [25] by the removal of hydrogen chloride from *cis*-β-chlorodecalin obtained from the decalol. These substances are oxidised to *trans*- and *cis*-*cyclo*hexanediacetic acids (V). By heating the chlorination product of decalin with aniline, however, the same authors obtained a slightly impure specimen of the Δ^1-octahydronaphthalene, presumably a mixture of isomerides, giving as principal oxidation product 1-carboxy*cyclo*hexane-2-propionic acid (I).

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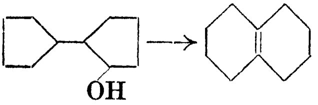
[22] E. V. Bell, G. M. Bennett, and F. G. Mann, *J.*, 1929, 1462; *A.*, 1929, 1042.

[23] F. D. Chattaway and E. G. Kellett, *J.*, 1930, 1352; *A.*, 1022.

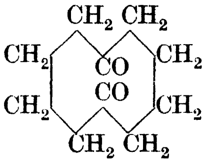
[24] *Ann. Chim.*, 1910, **21**, 458; *Compt. rend.*, 1910, **157**, 384; *A.*, 1910, ii, 828.

Both *cis*- and *trans*-Δ^2-isomerides may be obtained by the dehydration of the respective β-decalols with potassium bisulphate.[26]

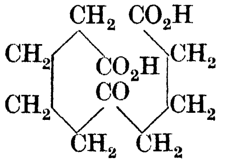
Attempts had been made to prepare the Δ^9-isomeride by nitrating decalin with boiling dilute nitric acid, reducing the resulting 9-nitrodecalin to the amino-compound, and decomposing this with nitrous acid.[27] The researches of W. Hückel and his assistants indicate that this method yields a mixture.[28] The pure substance has now been prepared and its structure carefully established. It may be obtained, by a complex reaction involving more than one rearrangement, by the dehydration of 2-*cyclo*pentyl*cyclo*pentanol (VI) (*cis* or *trans*) with zinc chloride. It has also been separated from the mixture of isomeric octahydronaphthalenes (produced by the dehydration of decalol with zinc chloride) in the form of its blue crystalline nitrosochloride, and is regenerated from this by the action of sodium methoxide.



(VI.)



(VII.)



(VIII.)

The structure of this octahydronaphthalene is confirmed by its conversion by ozone in acetic acid into *cyclo*decane-1 : 6-dione (VII) and δ-ketosebacic acid (VIII).

(2) *Decalin-β-spirans.* In the course of a study of spiran formation in this series K. A. N. Rao [29] has realised a number of cases of

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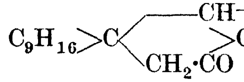
[25] *Annalen*, 1923, **434**, 219; *A.*, 1924, i, 32.

[26] W. Hückel and H. Friedrich, *Annalen*, 1926, **451**, 132; *A.*, 1927, 239; compare F. Eisenlohr and R. Polenske, *Ber.*, 1924, **57**, [*B*], 1639; *A.*, 1924, i, 1291.

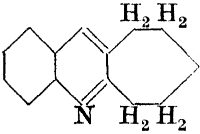
[27] S. Nametkin and others, *Ber.*, 1926, **59**, [*B*], 370; 1929, **62**, [*B*], 1570; *A.*, 1926, 508; 1929, 921.

[28] W. Hückel, R. Danneel, A. Schwartz, and A. Gercke, *Annalen*, 1929, **474**, 121; **477**, 99; *A.*, 76, 206.

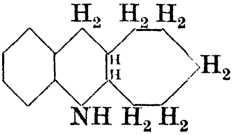
[29] *Loc. cit.* (Ref. 11; p. 155).

complicated isomerism. Substances of the type $C_9H_{16}{>}C{<}\substack{X\\Y}$ derived from *cis-* and *trans*-decalins should occur in four isomeric forms, two from each of the isomeric decalones. Two β-decalin-2 : 2′-diacetic acids (X = Y) were prepared, a single substance from each ketone, and each gave an anhydride. Their anilic acids, however, (X and Y different) involve the additional isomerism and all four forms of $C_9H_{16}{>}C{<}\substack{CH_2\cdot CO_2H\\CH_2\cdot CO\cdot NHPh}$ were separated, passing by loss of water into two anils, $C_9H_{16}{>}C{<}\substack{CH_2\cdot CO\\CH_2\cdot CO}{>}NHPh$. The decalin-β-*spirocyclo*propane-1 : 2-dicarboxylic acids and the derived lactonic acids  $C_9H_{16}{>}C{<}\substack{CH{-}CO_2H\\CH_2\cdot CO}{>}O$ were also studied, and of the latter all four possible isomerides from one decalone were isolated.

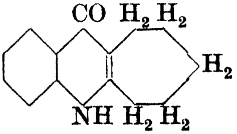
(3) *Octahydroheptaquinolines.* The variation in the proportions of two stereoisomerides produced in different methods of reduction of heterocyclic bases was referred to in the last Report (*Ann. Reports*, 1929, **26**, 165). In the light of this fact the reduction of tetrahydroheptaquinoline (I) has been repeated,[30] and it is now found that the use of sodium and alcohol produces a second isomeric octahydro-base (II) in addition to that already described.[31] The resulting knowledge of the properties of these substances has led to the detection of this second isomeride in the product of reduction by tin and hydrochloric acid and in the reduction product of the keto-compound (III).



(I.)



(II.)



(III.)

Molecular Dissymmetry.—Allene, spiran, and related types. A direct demonstration of the enantiomorphism of a single allene as foreseen by J. H. van 't Hoff is still lacking, and the view that the four terminal valencies in allene are co-planar was recently advanced[32] on the ground of the homogeneity of a substance described as diethyl di-*l*-menthyl allenetetracarboxylate. It has been shown, however, that the substance is not an allene derivative at all.[33]

Several new instances have been reported of the separation into optically active forms of a compound belonging to the fascinatingly symmetrical class of spirans. The resolution of *cyclo*butane*spiro*-*cyclo*butane-1 : 1-dicarboxylic acid (I) is due to H. J. Backer and H. B. J. Schurink,[34] and the compounds (II—V) have been shown to be enantiomorphous by J. Böeseken and his assistants.[35]

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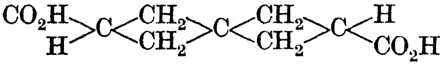
[30] S. G. P. Plant and R. J. Rosser, *J.*, 1930, 1840; *A.*, 1297.

[31] *Ann. Reports*, 1928, **25**, 184.

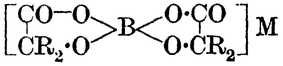
[32] F. Faltis, J. Pirsch, and L. Bermann, *Ber.*, 1930, **63**, [*B*], 691; *A.*, 578.

[33] C. K. Ingold and C. W. Shoppee, *J.*, 1930, 1619; *A.*, 1163.



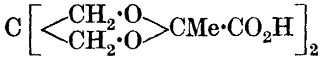
$$\begin{matrix}CO_2H\\H\end{matrix}\!>\!C\!<\!\begin{matrix}CH_2\\CH_2\end{matrix}\!>\!C\!<\!\begin{matrix}CH_2\\CH_2\end{matrix}\!>\!C\!<\!\begin{matrix}H\\CO_2H\end{matrix}$$

(I.)



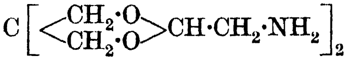
$$\left[\begin{matrix}CO-O\\CR_2\cdot O\end{matrix}\!>\!B\!<\!\begin{matrix}O\cdot CO\\O\cdot CR_2\end{matrix}\right]M$$

(II.)



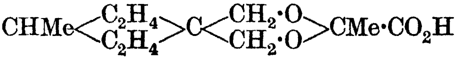
$$C\left[<\begin{matrix}CH_2\cdot O\\CH_2\cdot O\end{matrix}\!>\!CMe\cdot CO_2H\right]_2$$

(III.)



$$C\left[<\begin{matrix}CH_2\cdot O\\CH_2\cdot O\end{matrix}\!>\!CH\cdot CH_2\cdot NH_2\right]_2$$

(IV.)



$$CHMe\!<\!\begin{matrix}C_2H_4\\C_2H_4\end{matrix}\!>\!C\!<\!\begin{matrix}CH_2\cdot O\\CH_2\cdot O\end{matrix}\!>\!CMe\cdot CO_2H$$

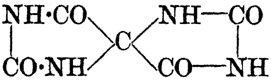
(V.)

The potassium borotartrate isolated by T. M. Lowry is probably of the same type.[36]

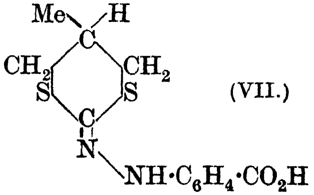
The recorded rotatory powers of those of the above compounds with spiran carbon as centre are very small. Apart from the probability of ready racemisation, it may be noted that the optical rotatory powers of substances of such complete symmetry and saturation in the immediate vicinity of the central atom are to be expected to be exceptionally small.

A heterocyclic spiran of remarkably simple type has been resolved by Sir W. J. Pope and J. B. Whitworth.[37] The rotation of this *spiro*-5 : 5-dihydantoin (VI) is reversed in sign in ammoniacal solution, probably owing to enolisation in salt formation.

The announcement has been made of the resolution of the *o*-carboxyphenylhydrazone of methyltrimethylenedithiocarbonate (VII) by W. H. Mills and B. C. Saunders.[38]



(VI.)



This new and clear evidence of the non-planar disposition of the valencies of the doubly linked nitrogen atom is of particular importance owing to the possible alternative explanation of the dissymmetry of the pyridylhydrazone of *cyclo*hexylene dithiocarbonate resolved in 1923.[39]

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[34] *Proc. K. Akad. Wetensch. Amsterdam*, 1928, **31**, 370; *A.*, 1928, 1134.

[35] *Rec. trav. chim.*, 1926, **45**, 919; *Ber.*, 1929, **62**, [*B*], 1310; *A.*, 1927, 132; 1929, 791; compare *Ann. Reports*, 1929, **26**, 74.

[36] *J.*, 1929, 2853; *A.*, 135. Compare E. Darmois, *J. Chim. physique*, 1930, **27**, 179; *A.*, 854.

[37] *Chem. and Ind.*, 1930, **49**, 748.

[38] *Trans. Faraday Soc.*, 1930, **26**, 431; *A.*, 1095.

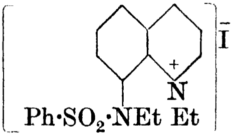
Dissymmetry due to restricted rotation. This field of work continues to attract considerable attention. The past year has seen the extension of the phenomenon to a quinoline derivative and the realisation of the diastereoisomerism consequent on its occurrence twice in the same molecule.

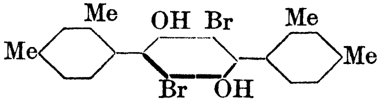
A quaternary salt derived from 8-benzenesulphonylethylaminoquinoline has been resolved with the aid of bromocamphorsulphonic acid by W. H. Mills and J. G. Breckenridge,[38] the optically active iodide (I) being obtained.

In the diphenyl series the following have been resolved : 2 : 4-dinitro-2′-methyldiphenyl-6-carboxylic acid (corresponding acids with the methyl group absent or in position 3′ could not be resolved),[40] 2 : 4 : 6 : 2′ : 4′ : 6′-hexanitrodiphenyl-3 : 3′-dicarboxylic acid, and 2 : 4 : 6 : 2′ : 4′-pentanitrodiphenyl-3-carboxylic acid.[41] A general review of this type of isomerism has been given with an analysis of the possibilities of interference of various atoms and groups judged from their dimensions as ascertained from *X*-ray crystal data.

The inactive diastereoisomerides (II) and (III) have been isolated by E. Browning and R. Adams,[42] which are oxidised to a common quinone. The obstruction of rotation thus disappears with the removal of two hydrogen atoms and the change of the central nucleus to the quinonoid form.

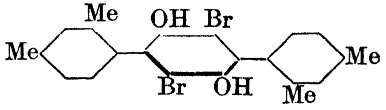
(I.)





(II.)

(III.)



Stereoisomerism of Co-ordination Compounds.—Optical activity dependent on 6-co-ordinated copper has been realised by W. Wahl [43] in the diethylenediaminediaquocupric salts, of which the active ion is estimated to have $[M] = -190°$. Indications of a similar optically active compound of 6-co-ordinated nickel were obtained.

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[39] *Ann. Reports*, 1927, **24**, 99.

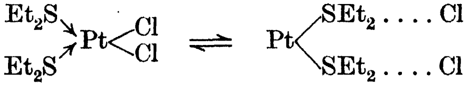
[40] (Miss) M. S. Lesslie and E. E. Turner, *J.*, 1930, 1758; *A.*, 1287.

[41] R. Adams and others, *J. Amer. Chem. Soc.*, 1930, **52**, 1200, 2054, 2070, 2959, 447, 4528; *A.*, 762, 911, 914, 1180.

[42] *Ibid.*, 1930, **52**, 4098.

[43] *Acta Sci. Fennicæ Comm. Phys. Math.*, 1927, **4**, 1; *A.*, 1928, 395.

Structure of compounds of 4-co-ordinated platinum. The question of the planar or tetrahedral disposition of the valencies of 4-co-ordinated platinum was mentioned in the Report for 1927.[44] Since that time the idea that the arrangement of the four valencies of tellurium is planar has been abandoned.[45] F. G. Angell, H. D. K. Drew, and W. Wardlaw have now reinvestigated the two isomeric complexes of platinous chloride with diethyl sulphide, described by Blomstrand in 1888, and regarded as of *cis-* and *trans*-planar configurations by A. Werner, and conclude that these are structural isomerides and that there is consequently no need for a special stereochemical hypothesis to account for them.[46] Formulæ (I) and (II) are now proposed :



(I.) α-Dichloride. (II.) β-Dichloride.

The α-dichloride is less polar, being insoluble in water; the β-isomeride is appreciably soluble in water, the solution being conducting. By the action of moist silver oxide, the β-dichloride yields a strong base, $Pt(SEt_2{\cdot}OH)_2$, from which an oxalate and other salts are obtained. The α-dichloride, on the other hand, is slowly but completely decomposed by silver oxide.

The tetrahedral configuration for the α-dichloride is supported by experiments on the addition of halogens to these substances, the results of which are regarded as definitely inconsistent with Werner's formulation. By implication doubt is also cast on the nature of the isomerism of the platinosammines.

On the other hand the problem why the ionisable chlorine in the β-dichloride (II) does not rapidly co-ordinate with the platinum atom to yield the α-isomeride (I) remains to be elucidated.

Moreover, a review by T. M. Lowry[47] of the results of *X*-ray investigations of crystals of complex compounds from this point of view suggests that caution is necessary in accepting the new formulæ. This author contends that the anions in the tetragonal crystals of the salt K_2PtCl_4 are undoubtedly of planar configuration as compared with the tetrahedral anions in the cubic $K_2Zn(CN)_4$.[48] Consequently the planar configuration for other complexes of 4-co-ordinated platinum should not be regarded as improbable.

Stereochemistry of the atom co-ordinated to a metal. In view of the discovery of optically active complexes of the metals by A. Werner, and of the fact that the distinction between principal and auxiliary valencies has been abandoned for some time, the stereochemical reality of the co-ordination bond might be regarded as obvious. Yet it is only in recent years that attention has been paid to the steric environment of the non-metallic atoms such as nitrogen and sulphur through which co-ordination to a metal takes place.

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[44] *Ann. Reports*, 1927, **24**, 104.

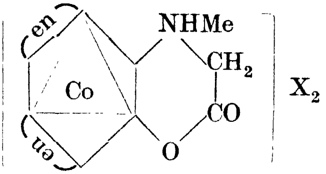
[45] *Ibid.*, 1929, **26**, 80; this vol., p. 150.

[46] *J.*, 1930, 349; *A.*, 559.

[47] *Proc. Camb. Phil. Soc.*, 1929, **25**, 219; *A.*, 1929, 629.

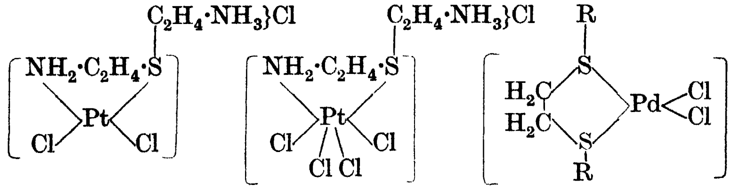
[48] R. G. Dickinson, *J. Amer. Chem. Soc.*, 1922, **44**, 774, 2404; *A.*, 1922, i, 532; 1923, ii, 25.

J. Meisenheimer in 1924 [49] obtained evidence of the existence of two optically active diastereoisomerides of the sarcosinediethylenediaminecobalt salts (I) and accounted for their existence by the supposition that in this case the nitrogen atom forms a second centre of dissymmetry in addition to the cobalt atom. It may be pointed out, incidentally, that if this explanation is correct the compound is an unusual one in another respect, for a hydrogen atom is attached to nitrogen, whereas the optical resolution of compounds of the type $[NHR^1R^2R^3]X$ has not been observed. The stereochemistry of the nitrogen and sulphur atoms in certain complexes has also been discussed by H. Reihlen.[50]



(I.)

The first case of optical activity solely due to this cause has been described recently by F. G. Mann.[51] The complex (II) resisted resolution, but when the platinum was oxidised to the 6-co-ordinated condition the resulting complex was successfully separated with the aid of camphor-10-sulphonic acid and the salt (III) was obtained having $[M]_{5461} + 1110°$.



(II.) (III.) (IV.)

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[49] *Annalen*, 1924, **438**, 217; *A.*, 1924, i, 1035.

[50] *Z. anorg. Chem.*, 1926, **151**, 71; *Annalen*, 1926, **447**, 211; **448**, 312; *A.*, 1926, 457, 699, 888.

[51] *J.*, 1930, 1745; *A.*, 1404.

The dissymmetry is here centred in the co-ordinated sulphur atom and arises from the non-planar distribution of its three bonds, which are disposed as in sulphonium salts and sulphoxides. An examination of some chelate complexes of the type of (IV) for the presence of the expected pairs of diastereoisomerides (here *cis* and *trans* with respect to the heterocyclic ring) was unsuccessful.[52] This corresponds with the failure of the resolution of the platinous complex (II) and may be attributed to the instability of the co-ordination bond, with consequent ready interconversion of the isomerides.

Natural Products.[53]

Owing to pressure of space an account will be given under this heading of three subjects only, namely, the chemistry of angustione, carotene, and santonin. Other topics are held over until next year, when it is hoped to deal with recent work on the sterols and bile acids.

Angustione.—A naturally occurring β-diketone has been found for the first time in angustione from the essential oil of *Backhousia angustifolia.*[54] The substance, which has the composition $C_{11}H_{16}O_3$, shows an intense ferric chloride coloration, readily yields a copper derivative, and by the action of ammonia an amino-compound. The action of alcoholic potassium hydroxide at 150° causes fission into acetic acid and a diketone, $C_9H_{14}O_2$. This is of the substituted dihydroresorcinol class, yields ααγ-trimethylglutaric acid on treatment with sodium hypobromite, and is therefore 1 : 1 : 3-trimethyl*cyclo*hexane-4 : 6-dione (I). The unsaturated compound (II), obtained by oxidation of (I) or of angustione with ferric chloride, is itself oxidised to dimethylmalonic acid and is converted by phosphorus trichloride into 4 : 6-dichloro-1 : 2 : 3-trimethylbenzene.[55]

Angustione is therefore a triketone of the formula (III). There is found with it a second diketonic substance, dehydroangustione (IV), which is transformed into the unsaturated diketone (II) by the action of 50% sulphuric acid. This unusual structure for dehydroangustione has been confirmed by its oxidation to ααγ-trimethylglutaconic acid[55a] and a β-hydroxy-ααγ-trimethylglutaric acid (V).

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[52] G. M. Bennett, A. N. Mosses, and F. S. Statham, *J.*, 1930, 1668; *A.*, 1432.

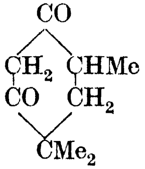
[53] Mention should have been made in the last Report (p. 145) of the important addition to C. A. Kerr's synthesis of norpinic acid made by C. W. Shoppee and J. L. Simonsen (*Chem. and Ind.*, 1929, **48**, 730), who converted the synthetic *trans*-acid into the *cis*-acid identical with that from pinene.

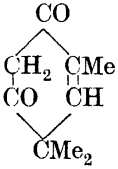
[54] A. R. Penfold, *J. Proc. Roy. Soc. New South Wales*, 1923, **57**, 300; C. S. Gibson, A. R. Penfold, and J. L. Simonsen, *J.*, 1930, 1184; *A.*, 1924, i, 1328; 1930, 921.

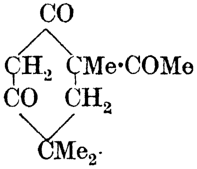
[55] Compare *Ann. Reports*, 1906, **3**, 122.

[55a] Private communication.

These substances thus contain the "ionone" ring which has recently been found in carotene (see below). They possess a carbon skeleton which evidently is not a simple multiple of the isoprene unit, but the problem of their genesis is an interesting one and it may perhaps be assumed that at least two molecules of isoprene are involved.


(I.)


(II.)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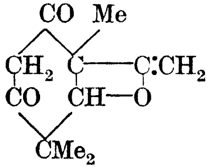
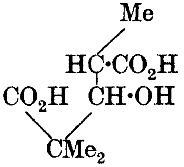

(IV.)


(V.)

Carotene and Lycopene.—Recent biochemical work in connexion with vitamin-*A* [56] having shown the importance of carotene, the elaboration of a formula for this substance by P. Karrer and his associates is of exceptional interest.

Carotene is a yellow hydrocarbon, $C_{40}H_{56}$, found in the carrot and in the leaves and seeds of many plants; it is the colouring matter of butter. The substance was isolated with chlorophyll from stinging nettles by R. Willstätter and W. Mieg in 1907.[57] The isomeric lycopene (which also gives the colour reaction for vitamin-*A*) was obtained from tomatoes and rose hips.[58] The latter hydrocarbon is aliphatic, for complete hydrogenation converts it into the paraffin $C_{40}H_{82}$.[59] The formula

$$CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH[CH{:}CH{\cdot}CMe{:}CH]_5CH_2{\cdot}CH_2{\cdot}CMe{:}CHMe$$

was proposed for lycopene [60] and received some justification from oxidation experiments.

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[56] *Ann. Reports*, 1929, **26**, 245; H. N. Green and E. Mellanby, *Brit. J. Exp. Path.*, 1930, **11**, 81.

[57] *Annalen*, 1907, **355**, 1; *A.*, 1907, i, 865.

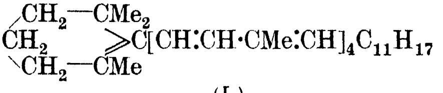
[58] R. Willstätter and H. H. Escher, *Z. physiol. Chem.*, 1910, **64**, 52; H. H. Escher, *Helv. Chim. Acta*, 1928, **11**, 752; *A.*, 1910, i, 330; 1928, 1016.

[59] P. Karrer and R. Widmer, *Helv. Chim. Acta*, 1928, **11**, 751; *A.*, 1928, 1016.

[60] P. Karrer and W. E. Bachmann, *ibid.*, 1929, **12**, 285; *A.*, 1929, 569. P. Karrer, A. Helfenstein, and H. Wehrli, *ibid.*, 1930, **13**, 87; *A.*, 333.

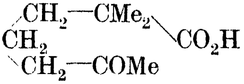
Catalytic hydrogenation and other tests showed that the carotene molecule contained eleven double bonds with three (or two) less reactive than the others,[61] the ultimate reduction product being of composition $C_{40}H_{78}$. It is therefore dicyclic.

The nature of one ring in carotene was indicated by the production from it by the action of cold permanganate of a substance identical with ionone and yielding, like ionone, *as*-dimethylsuccinic acid on oxidation.[62] It follows that the molecule contains the trimethyl*cyclo*hexene ring of ionone, and the partial formula (I) was adopted.



$$\begin{array}{l}\diagup CH_2{-}CMe_2\\ CH_2 \qquad {>}C[CH{:}CH{\cdot}CMe{:}CH]_4C_{11}H_{17}\\ \diagdown CH_2{-}CMe\end{array}$$

(I.)

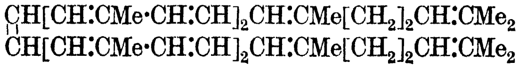


$$\begin{array}{l}\diagup CH_2{-}CMe_2\diagdown\\ CH_2 \qquad\qquad CO_2H\\ \diagdown CH_2{-}COMe\end{array}$$

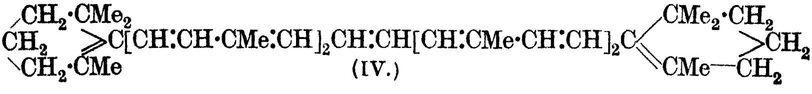
(II.)

In the latest memoir [63] the isolation of other oxidation products is described, including geronic acid (II), confirming the presence of the ionone ring. As the second ring of carotene, contained in the residue $C_{11}H_{17}$ in formula (I), is likely to have resulted from ring-closure in the lycopene molecule, this residue would (from the structure assumed for lycopene) be of the form $-CH{:}CH{\cdot}CMe{<}\begin{smallmatrix}CH_2-CH_2\\ CMe{:}CMe\end{smallmatrix}{>}CH_2$. But none of the expected oxidation products of such a ring is detected, nor is carotene optically active as it would then presumably be. A careful study of the proportions of acetic acid resulting from oxidation of lycopene and carotene with chromic acid moreover shows that each yields 6 mols. of acetic acid per mol., whereas these formulæ require 8 and 7 mols. respectively (one for each C–CMe:C group).

These difficulties are now surmounted by adopting the formulæ (III) and (IV) for the two hydrocarbons :

(III.) 

$$\begin{array}{l}CH[CH{:}CMe{\cdot}CH{:}CH]_2CH{:}CMe[CH_2]_2CH{:}CMe_2\\ \|\\ CH[CH{:}CMe{\cdot}CH{:}CH]_2CH{:}CMe[CH_2]_2CH{:}CMe_2\end{array}$$



$$\begin{array}{l}\diagup CH_2{\cdot}CMe_2 \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \diagup CMe_2{\cdot}CH_2\\ CH_2 \quad {>}C[CH{:}CH{\cdot}CMe{:}CH]_2CH{:}CH[CH{:}CMe{\cdot}CH{:}CH]_2C \qquad {>}CH_2\\ \diagdown CH_2{\cdot}CMe \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \diagdown CMe{-}CH_2\end{array}$$

(IV.)

The second ring in (IV), being equally an ionone ring, gives rise to no other oxidation products.

It is noticeable that the formulæ no longer represent products of continuous polymerisation of isoprene, but it is suggested that the lycopene carbon chain may arise by the union of two molecules of phytol aldehyde. Phytol, the alcohol of chlorophyll, has recently been identified as 3 : 7 : 11 : 15-tetramethyl-Δ^2-hexadecen-1-ol, the constitution having been confirmed by a synthesis from ψ-ionone.[64] The corresponding aldehyde,

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[61] R. Pummerer and L. Rebmann, *Ber.*, 1928, **61**, [*B*], 1099; W. Reindel, *ibid.*, 1929, **62**, [*B*], 1411; L. Zechmeister and others, *ibid.*, 1928, **61**, [*B*], 566, 1534; 1929, **62**, [*B*], 2232; *A.*, 1928, 524, 765, 1015; 1929, 906, 1306.

[62] P. Karrer and A. Helfenstein, *Helv. Chim. Acta*, 1929, **12**, 1142; *A.*, 76.

[63] P. Karrer, A. Helfenstein, H. Wehrli, and A. Wettstein, *ibid.*, 1930, **13**, 1084; *A.*, 1422.

$$CHMe_2[CH_2]_3CHMe[CH_2]_3CHMe[CH_2]_3CMe{:}CH{\cdot}CHO,$$

by a benzoin condensation or a pinacol reduction would give the required carbon chain and dehydrogenation would lead to lycopene (III).

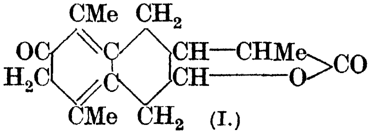
This argument has led the authors to suggest a corresponding alteration in the formula for squalene,[65] which would be

$$\{CMe_2{:}CH[CH_2]_2CMe{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH{\cdot}CH_2{\cdot}\}_2.$$

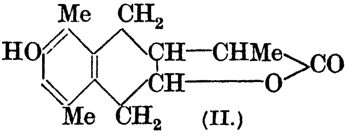
The ketone $C_{19}H_{38}O$ obtained by oxidation of partly reduced squalene should therefore be 2 : 6 : 10-trimethylhexadecan-15-one and not the 3 : 7 : 11-isomeride. The former has been synthesised and appears to be identical with the ketone from squalene.

Santonin.—This substance, which is the chief active constituent of wormseed, has long been known to be a lactone derived from a reduced naphthalene molecule. Its chemistry was developed particularly by S. Cannizzaro and his pupils and the formula (I) was generally accepted.

Santonin is ketonic but is converted by concentrated hydrochloric acid into a phenol, *desmotropo*santonin, hitherto written as (II), and drastic reduction yields santonous acid (III).



(I.)



(II.)

The question of the constitution of santonin has been reopened by G. R. Clemo, R. D. Haworth, and E. Walton,[66] who considered that the conversion into *desmotropo*santonin could not be merely a keto-enolic change, and that the santonin skeleton would more probably be such as could be derived by the union of isoprene units. The structure (IV) was suggested as meeting these and other points —in particular the observations of A. Angeli and L. Marino,[67] who obtained by oxidation a heptanetetracarboxylic acid, apparently possessing a quaternary carbon atom, to which formula (XX) may be assigned. The change to *desmotropo*santonin must on this view involve the migration of a methyl group—for which, however, there

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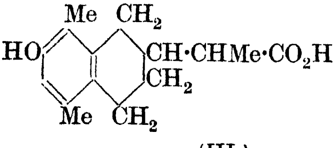
[64] F. H. Fischer and K. Löwenberg, *Annalen*, 1928, **464**, 69; 1929, **475**, 183; *A.*, 1928, 989; 1929, 1421.

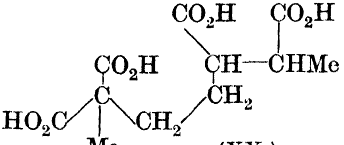
[65] *Ann. Reports*, 1929, **26**, 90.

[66] *J.*, 1929, 2368; 1930, 1110, 2579; *A.*, 1929, 1454; 1930, 919.

[67] *Atti R. Accad. Lincei*, 1907, **16**, i, 159; *Mem. Accad. Lincei*, 1908, **6**, 385; *A.*, 1907, i, 321; 1908, i, 543.

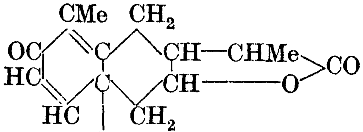


(III.)

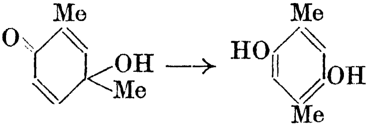


(XX.)

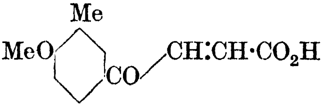
is a close analogy in the conversion of 2 : 4-dimethylchinol (V) into 2 : 5-dimethylquinol (VI).[68]



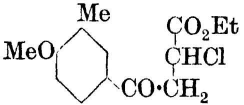
(IV.)



(V.) (VI.)

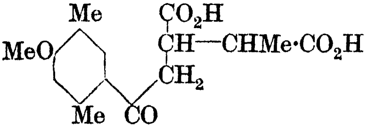


(VII.)

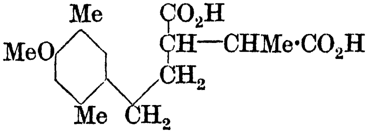


(VIII.)

The position of the α-propionic acid side-chain was first fixed by a synthesis of santonous acid. Condensation of *p*-xylyl methyl ether with maleic anhydride in presence of aluminium chloride gave the unsaturated acid (VII), which was converted by hydrogen chloride and ethyl alcohol into the ester (VIII). The latter by coupling with diethyl methylmalonate and hydrolysis yielded a mixture of stereoisomeric acids (IX), which were reduced by Clemmensen's method to two acids of structure (X). The action of sulphuric acid caused ring closure, and the product (XI) (obtained in an enol-lactonic form) by further reduction furnished *dl*-santonous acid methyl ether, which was demethylated to the acid itself (III).

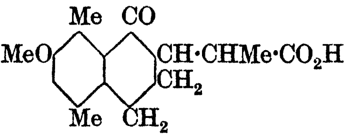


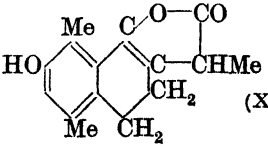
(IX.)



(X.)

(XI.)





(XII.)

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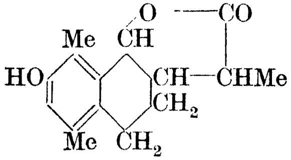
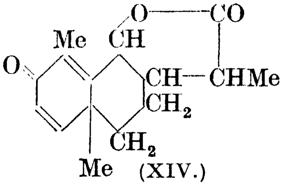
[68] E. Bamberger and F. Brady, *Ber.*, 1900, **33**, 3642; *A.*, 1901, i, 142.

This confirmed the accepted formula for santonous acid, and that for *desmotropo*santonin was next proved by synthesis. One of the acids (X) yielded, when heated with hydriodic acid, the enol-lactone (XII), and sodium amalgam reduced this to *desmotropo*santonin (XIII). This formula differs from (II) only in the position of the lactone ring. Such an oblique arrangement of rings had been suggested by S. Cannizzaro.[69] It entails a readjustment of the santonin formula to (XIV).

Evidence was still needed of the position of the methyl group regarded as migrating, and it was obtained as follows. Tetrahydrosantonin, resulting from catalytic hydrogenation, was reduced by Clemmensen's method to the fully saturated lactone, from which by the action of selenium a hydrocarbon was formed which proved to be 1-methyl-7-ethylnaphthalene [70] (XV).



(XIII.)



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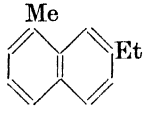

(XV.)

The formula (XIV) for santonin has been accepted by L. Ruzicka,[71] who announced the degradation to 1-methyl-7-ethylnaphthalene a little before the other authors.

Santonin is thus placed in the eudesmol (selinene) group [72] of terpene compounds.

G. M. Bennett.
A. W. Chapman.

Part III.—Heterocyclic Division.

Oxygen Ring Compounds.

An account was given in last year's Report [1] of the preparation of various flavones, flavonols, etc., by the acylation of *o*-hydroxyacetophenone derivatives. This process has now been further applied by A. Lovecy, R. Robinson, and S. Sugasawa [2] to the synthesis of luteolin 3′- and 4′-methyl ether (I and II respectively) by acting upon phloracetophenone with sodium *O*-benzylvanillate and *O*-benzylvanillic anhydride, on the one hand, and sodium *O*-benzyl*iso*vanillate and *O*-benzyl*iso*vanillic anhydride on the other, followed by the hydrolysis of the primary products in each

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[69] *Ber.*, 1893, **26**, 786; *A.*, 1893, i, 364.

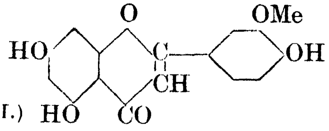
[70] J. Harvey, I. M. Heilbron, and D. G. Wilkinson, *J.*, 1930, 423; *A.*, 593.

[71] L. Ruzicka and E. Eichenberger, *Helv. Chim. Acta*, 1930, **13**, 1117; *A.*, 1442.

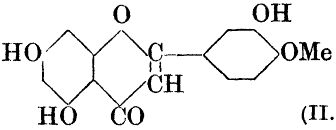
[72] *Ann. Reports*, 1923, **20**, 100; 1924, **21**, 103.

[1] *Ann. Reports*, 1929, **26**, 152.

[2] *J.*, 1930, 817.

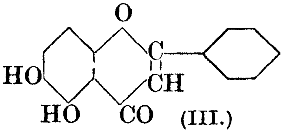


(I.)

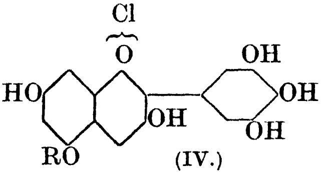


(II.)

case. The latter flavone (II) was found to be identical with diosmetin, the rhamnoglucoside of which is diosmin, recently isolated by O. A. Oesterle and G. Wander.[3] An examination of the reactions of primetin, from *Primula modesta,* has led W. Nagai and S. Hattori [4] to the conclusion that it is 5 : 6-dihydroxyflavone (III). The presence of an unsubstituted 2-phenyl group is indicated by the formation of benzoic acid on alkali fission, and the vicinal character of the two hydroxyl groups is suggested by a green coloration with ferric chloride and the readiness with which oxidation can occur. Primetin can give a diacetyl derivative, but methylation with diazomethane or methyl iodide and alkali leads to a monomethyl ether, which gives a violet-brown colour with ferric chloride and can be acetylated. The formula (III) for primetin is further supported by an investigation of the absorption spectrum.

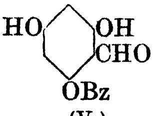


(III.)

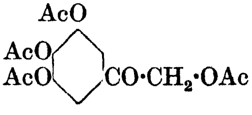


(IV.)

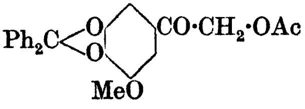
Some of the earlier syntheses of well-known anthocyanidins through their methyl ethers have proved to be unsatisfactory, since the subsequent demethylation process led to impure products, and in more recent times they have been replaced in certain cases by much improved methods which avoid demethylation.[5] These later reactions have now been applied by W. Bradley, R. Robinson, and G. Schwarzenbach [6] to the preparation of delphinidin chloride (IV ; R = H). The interaction of 2-*O*-benzoylphloroglucinaldehyde



(V.)



(VI.)



(VII.)

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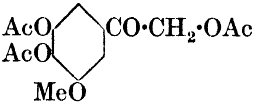
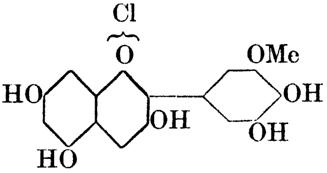
[3] *Helv. Chim. Acta,* 1925, **8**, 519.
[4] *Acta Phytochim.*, 1930, **5**, 1; *A.*, 784.
[5] See *Ann. Reports,* 1928, **25**, 163.
[6] *J.*, 1930, 793.

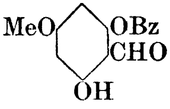
(V) and ω : 3 : 4 : 5-tetra-acetoxyacetophenone (VI) by means of hydrogen chloride in alcohol–ethyl acetate yielded 5-*O*-benzoyldelphinidin chloride (IV; R = Bz), the acetyl groups being removed during the reaction. Hydrolysis with aqueous-alcoholic sodium hydroxide and subsequent treatment with hydrochloric acid then gave a product which was identical with delphinidin chloride from natural sources. A similar series of reactions with (V) and either (VII) or (VIII) led ultimately to 3′-*O*-methyldelphinidin chloride (IX), which very closely resembled natural petunidin chloride, although complete identity was not established, possibly owing to the disturbing effects of traces of impurity in the natural product. The same authors have condensed 2-*O*-benzoyl-4-*O*-methylphloroglucinaldehyde (X) with ω-acetoxy-4-benzyloxy-3 : 5-dimethoxyacetophenone (XI) by an analogous process, and, after hydrolysis of the resulting 5-*O*-benzoyl derivative, 7 : 3′ : 5′-*O*-trimethyldelphinidin chloride (XII) was obtained. This substance proved to be identical with hirsutidin chloride, recently isolated from *Primula hirsuta*,[7] so that the structure of this anthocyanidin is now definitely established.



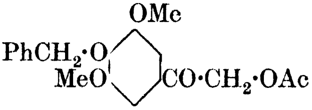
(VIII.)



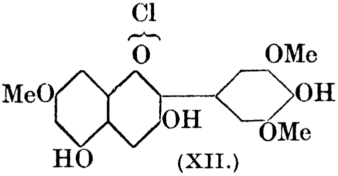
(IX.)



(X.)



(XI.)



(XII.)

One of the most interesting problems associated with the naturally occurring oxygen ring compounds is the interconversion of the various types. Several processes of this nature have already received considerable attention,[8] and R. Robinson and G. Schwarzenbach [9] have now made a study of the conversion of flavylium salts into flavones. Although this change is reminiscent of the facile transformation of an alkylpyridinium salt to a pyridone, no successful general procedure has hitherto been developed for it.

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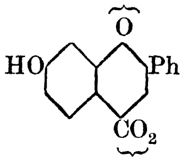
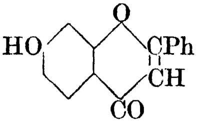
[7] P. Karrer and R. Widmer, *Helv. Chim. Acta*, 1927, **10**, 758.

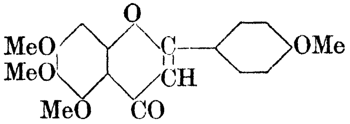
[8] See *Ann. Reports*, 1928, **25**, 169.

[9] *J.*, 1930, 822.

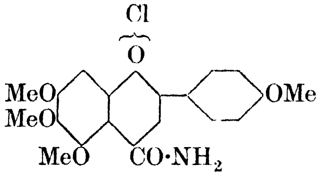
7-Hydroxy-4-carboxyflavylium betaine (XIII) has been oxidised to 7-hydroxyflavone (XIV) by the use of chromic acid in acetic acid

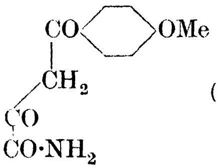

(XIII.)


(XIV.)

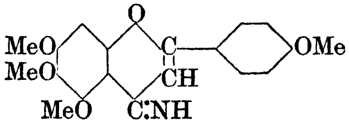

(XV.)

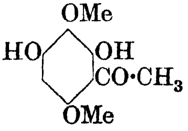
solution,[10] but the method cannot be applied in general to related 4-carboxyflavylium salts or the corresponding betaines. It has been found, however, that scutellarein tetramethyl ether (XV) can be synthesised by an application of the Hofmann reaction to the appropriate acid amide of this type. The 4-carbamyl-5 : 6 : 7 : 4′-tetramethoxyflavylium chloride (XVI) resulting from the interaction of anisoylpyruvamide (XVII), antiarol (3 : 4 : 5-trimethoxyphenol), and hydrogen chloride was submitted to a Hofmann reaction and yielded a pseudo-base (XVIII) which was subsequently converted into the tetramethoxyflavone (XV) by treatment with boiling

(XVI.)



(XVII.)

dilute aqueous sodium hydroxide. The authors point out that, if an easily accessible route can be found for the preparation of the aroylpyruvamides, this might become a valuable method for the synthesis of flavones. The preceding preparation of scutellarein tetramethyl ether is of added interest in view of the fact that the earlier synthesis of this flavone by G. Bargellini [11] involved a process which was not quite unambiguous. An alternative synthesis has more recently been described by F. Wessely and G. H. Moser.[12] The action of anisic anhydride and potassium anisate on 2 : 4-dihydroxy-3 : 6-dimethoxyacetophenone (XIX) at 180—185°, followed


(XVIII.)


(XIX.)

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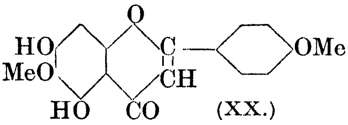
[10] C. Bülow and H. Wagner, *Ber.*, 1903, **36**, 1941.

[11] *Gazzetta*, 1915, **45**, 69.

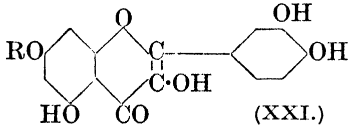
[12] *Monatsh.*, 1930, **56**, 97; *A.*, 1295.

by hydrolysis of the primary product, resulted in the unexpected formation of 5 : 7-dihydroxy-6 : 4′-dimethoxyflavone (XX), which involved partial demethylation. The tetra-acetate of the 5 : 6 : 7 : 4′-tetrahydroxyflavone obtained by the demethylation of the latter product proved to be identical with scutellarein tetra-acetate.

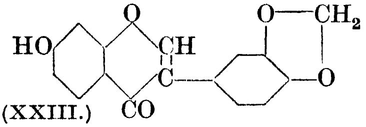
There now appears to be some doubt whether the reduction of flavonols in acid solution can actually lead to anthocyanidins as previously believed.[13] The product obtained from quercetin (XXI; R = H), although it closely resembles cyanidin chloride, is regarded by T. Malkin and M. Nierenstein [14] as having the constitution (XXII), and an analogous structure is assigned to the product of the reduction of rhamnetin (XXI; R = Me).



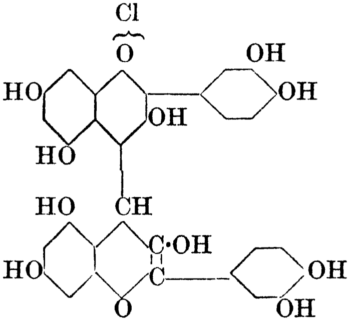
(XX.)



(XXI.)

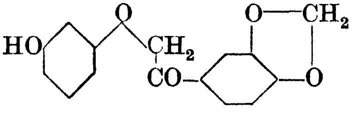


(XXIII.)

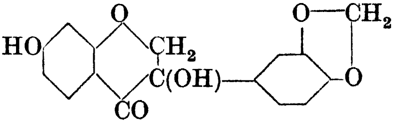


(XXII.)

It was mentioned in last year's Report [15] that ψ-baptigenin had been recognised as an *iso*flavone of the formula (XXIII). The constitution assigned to this product has now been confirmed synthetically in two ways by E. Späth and E. Lederer.[16] In the first route, the crude cyanohydrin of the substance (XXIV), which was obtained by condensing resorcinol and ω-bromoacetopiperone in the presence of sodium hydroxide, was submitted to a Hoesch



(XXIV.)



(XXV.)

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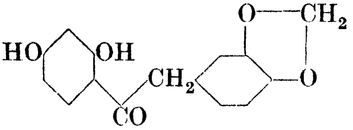
[13] R. Willstätter and H. Mallison, *Sitzungsber. K. Akad. Wiss. Berlin*, 1914, 769; *A.*, 1914, i, 1081; A. Robertson and R. Robinson, *J.*, 1927, 2196.

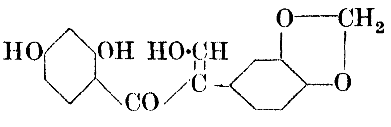
[14] *J. Amer. Chem. Soc.*, 1930, **52**, 2864; *A.*, 1189.

[15] *Ann. Reports*, 1929, **26**, 156.

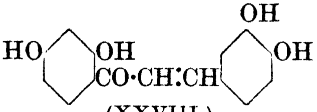
[16] *Ber.*, 1930, **63**, [*B*], 743; *A.*, 611.

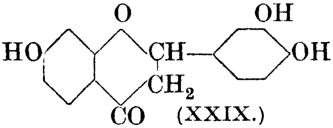
reaction, and the product, which undoubtedly contained the compound (XXV), was subsequently sublimed in a vacuum. Besides the unchanged ketone (XXIV), ψ-baptigenin, identical with the substance from natural sources, was obtained in this way. In the second method, ψ-baptigenetin (XXVI), previously synthesised from resorcinol and 3 : 4-methylenedioxyphenylacetonitrile by a Hoesch reaction, was treated with ethyl formate and sodium, and the product (XXVII) was heated with alcohol and fuming hydrochloric acid; after subsequent sublimation, ψ-baptigenin was again isolated.


(XXVI.)

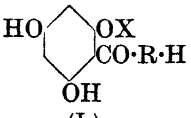

(XXVII.)

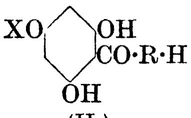
Using synthetical processes already well known in the chalkone and flavanone series,[17] J. Shinoda, S. Sato, and M. Kawagoe [18] have prepared butein (XXVIII) by first condensing resorcinol and 3 : 4-diethylcarbonatocinnamoyl chloride in nitrobenzene in the presence of aluminium chloride, and then heating the product with aqueous potassium hydroxide. On treatment with boiling alcoholic hydrochloric acid, butein was converted into the corresponding flavanone, butin (XXIX).

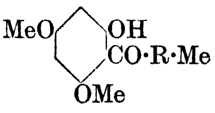

(XXVIII.)


(XXIX.)

Considerable attention has recently been directed towards the position of the sugar residue in certain well-known glucosides. The widely occurring product phloridzin yields phloretin and glucose on hydrolysis, but, although the structure of phloretin has long been established and it has been known that the glucose residue is attached to the phloroglucinol nucleus, its exact location has been uncertain,


(I.)


(II.)


(III.)

($X = C_6H_{11}O_5$; $R = \cdot CH_2\cdot CH_2\cdot C_6H_4\cdot O\cdot$)

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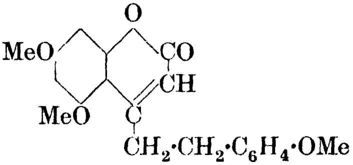
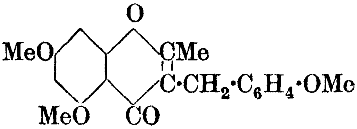
[17] See, *e.g.*, J. Shinoda and S. Sato, *J. Pharm. Soc. Japan*, 1928, **48**, 109; *Ann. Reports*, 1928, **25**, 169.

[18] *J. Pharm. Soc. Japan*, 1929, **49**, 123; *A.*, 1930, 93.

the formulæ (I) and (II) both being possible. This point has now been settled by an examination of the product obtained by hydrolysing the fully methylated glucoside.[19] This product must have the structure (III), since, on heating with acetic anhydride and sodium acetate, acetylation is accompanied by ring closure to give a substance which is either a coumarin (IV) or a chromone (V), a process



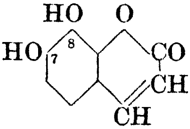
(IV.)



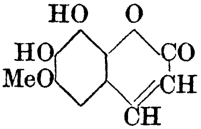
(V.)

which is dependent upon the presence of a free hydroxyl group in the 2-position with respect to the carbonyl group. Furthermore, the compound (III) has also been prepared by the catalytic hydrogenation of 2-hydroxy-4 : 6-dimethoxyphenyl *p*-methoxystyryl ketone. Phloridzin, therefore, has the constitution (I). Previous experience with analogous reactions indicates that the acylation product of the substance (III) is almost certainly the chromone (V), and this has recently been confirmed by J. Shinoda and T. Sato [20] from a study of the chemical behaviour of the compound.

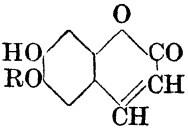
The glucoside obtained from β-acetobromoglucose and daphnetin [21] (VI) has been shown to have the glucose residue in the 8-position,[22] and S. Hattori [23] has now proved that it is not identical with daphnin, the naturally occurring glucoside of daphnetin. Furthermore, the methyldaphnetin obtained from the synthetic glucoside by methylation and subsequent hydrolysis was found to be different from the methyldaphnetin obtained by a similar process from daphnin.[24] It follows that daphnin must have the glucose residue in the 7-position.



(VI.)



(VII.)



(VIII.)

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[19] F. Wessely and K. Sturm, *Monatsh.*, 1929, **53** and **54**, 554; *A.*, 1929, 1452; F. R. Johnson and A. Robertson, *J.*, 1930, 21.

[20] *J. Pharm. Soc. Japan*, 1930, **50**, 32; *Chem. Zentr.*, 1930, ii, 404.

[21] P. Leone, *Gazzetta*, 1925, **55**, 674; *A.*, 1926, 75.

[22] F. Wessely and K. Sturm, *Ber.*, 1929, **62**, [*B*], 115; *A.*, 1929, 298.

[23] *J. Pharm. Soc. Japan*, 1930, **50**, 82.

[24] See also F. Wessely and K. Sturm, *Ber.*, 1930, **63**, [*B*], 1299.

Fraxin, the naturally occurring glucoside of fraxetin (VII), has been shown by F. Wessely and E. Demmer[25] from a series of alkylation experiments to have the glucose residue in the 8-position, for it is converted by successive methylation, hydrolysis, and ethylation into 6 : 7-dimethoxy-8-ethoxycoumarin, identical with the product obtained from 7-methoxy-8-ethoxycoumarin by oxidation[26] and subsequent methylation.

Although it has long been known that æsculin yields glucose and æsculetin on hydrolysis, and that the latter is 6 : 7-dihydroxycoumarin (VIII; R = H), the exact location of the glucose residue has again hitherto remained uncertain. F. S. H. Head and A. Robertson[27] have now shown that the glucosidoxy-group is in the 6-position (VIII; $R = C_6H_{11}O_5$). By successive methylation, hydrolysis, and ethylation, the glucoside yielded a methoxyethoxycoumarin, which was converted into the methyl ester of 2 : 4-dimethoxy-5-ethoxycinnamic acid by the subsequent action of methyl sulphate and sodium hydroxide. The structure of the acid derived from this ester on hydrolysis was confirmed by synthesis.

Mention may be made of several interesting observations in the chemistry of other oxygen ring compounds not directly related to natural products. An investigation by R. E. Lutz[28] into the reduction products of several unsaturated 1 : 4-diketones containing the group O:C·C:C·C:O has shown that they may consist of the corresponding saturated diketone, the corresponding furan derivative, or a mixture of these two, according to the conditions employed. The fact that the saturated 1 : 4-diketones are themselves unchanged by the conditions which lead to the furans suggests that the course of the formation of the furan ring involves first 1 : 6-addition of hydrogen to give the group HO·C:C·C:C·OH, followed by the elimination of water.

An interesting isomeric change has been brought to light by T. Reichstein,[29] who has shown that the action of aqueous potassium cyanide on 2-chloromethylfuran leads essentially to 5-cyano-2-methylfuran (I), only a small quantity of the corresponding 2-cyanomethylfuran (II) being formed. Hydrolysis of the mixed cyanides gave the analogous 2-methylfuran-5-carboxylic acid and furan-2-acetic acid.

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[25] *Ber.*, 1929, **62**, [*B*], 120; *A.*, 1929, 298.

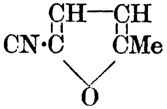
[26] Compare G. Bargellini, *Gazzetta*, 1916, **46**, 249; *A.*, 1916, i, 489.

[27] *J.*, 1930, 2434.

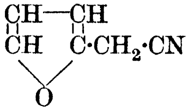
[28] *J. Amer. Chem. Soc.*, 1929, **51**, 3008; *A.*, 1929, 1459.

[29] *Ber.*, 1930, **63**, [*B*], 749; *A.*, 611; see also M. M. Runde, E. W. Scott, and J. R. Johnson, *J. Amer. Chem. Soc.*, 1930, **52**, 1284; *A.*, 783.

T. Reichstein[30] has also made a detailed study of the ease with which well-known aldehyde and ketone syntheses proceed in the furan series. Furfuraldehyde was obtained from furan by the action of anhydrous hydrocyanic acid and hydrogen chloride in ether at −15° without any additional condensing agent, the mixture being subsequently warmed to room temperature and the product decomposed with water. Similar experimental conditions resulted in the introduction of the α-aldehydo-group into several 2-alkylfurans, but the procedure failed when applied to 2-acetylfuran, ethyl pyromucate, coumarone, furfuryl methyl ether (III), and difurfuryl ether. These conditions also constituted a satisfactory method for the conversion of 1-alkylpyrroles into the corresponding 1-alkylpyrrole-2-aldehydes, but failed in the case of pyrrole itself, 2-acetylpyrrole, and pyrrole-2-carboxylic acid. The method also could not be applied to the preparation of thiophen-2-aldehyde, although this could be accomplished when an additional condensing agent was present, as, for example, when a mixture of thiophen, anhydrous hydrocyanic acid, and benzene was treated with aluminium chloride and hydrogen chloride. The 2-acetyl derivative of furan was prepared by the interaction of furan and acetyl chloride in benzene at 0° in the presence of stannic chloride; 2-acetyl-5-methylfuran also was obtained under similar conditions, but a better yield resulted from the use of zinc chloride and ether. The author has discussed the applicability of these experimental conditions and of those previously described by other workers in this field.



(I.)



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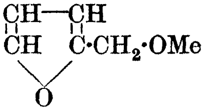

(III.)

It has been observed that 7-hydroxy-2 : 3-diphenylbenzo-γ-pyrone (IV) and some closely related derivatives dissolve in hot aqueous alkaline solutions and give gels on cooling, but only small changes in the nature of the substituents can be made without destroying this characteristic.[31] Owing to the possible value of a fluorescent gel-forming substance in the examination of the structure of gels, W. Baker[32] has prepared 10-hydroxyphenanthraxanthone (V), which, although closely related to (IV), contains a phenanthrene nucleus and so might be expected to exhibit fluorescence. The preparation was accomplished by an application of Pschorr's phenanthrene synthesis to the methyl ether of 7-hydroxy-3-phenyl-

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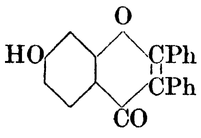
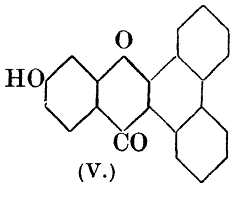
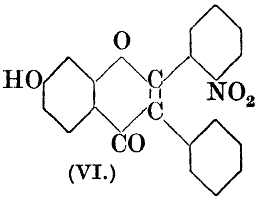
[30] *Helv. Chim. Acta*, 1930, **13**, 345, 349, 356; *A.*, 783, 787.

[31] W. Baker and R. Robinson, *J.*, 1925, **127**, 1981; W. Baker and (Miss) F. M. Eastwood, *J.*, 1929, 2897.

[32] *J.*, 1930, 261.


(IV.)

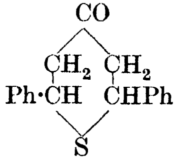

(V.)

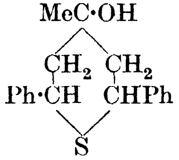

(VI.)

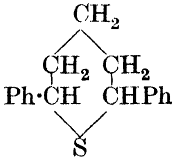
2-*o*-nitrophenylbenzo-γ-pyrone (VI), but the product gave a gel which showed no marked fluorescence and was not particularly stable.

Sulphur and Selenium Ring Compounds.

The configurations of the two stereoisomeric forms of 2 : 6-diphenylpenthian-4-one (I), isolated by F. Arndt, P. Nachtwey, and J. Pusch,[33] have now been established by F. Arndt and E. Schauder.[34] The modification (A), m. p. 113—114°, must be the *cis*-, since it gave two varieties of 2 : 6-diphenyl-4-methylpenthian-4-ol (II) on treatment with magnesium methyl bromide. These latter were


(I.)


(II.)


(III.)

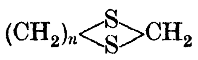
dehydrated to the same 2 : 6-diphenyl-4-methyl-Δ^3-penthiene (or 2 : 6-diphenyl-4-methylenepenthian). The modification (B), m. p. 87—88°, on similar treatment, gave first an amorphous product and then an isomeric diphenylmethylpenthiene. The two forms of (I) have been reduced by amalgamated zinc and hydrochloric acid to the corresponding *cis*- and *trans*-modifications of 2 : 6-diphenylpenthian (III). Penthian-4-one itself has been prepared by G. M. Bennett and L. V. D. Scorah[35] by the application of a Dieckmann reaction to ethyl β-thiodipropionate, $S(CH_2{\cdot}CH_2{\cdot}CO_2Et)_2$, and hydrolysis of the resulting ester.

Other interesting sulphur-containing rings are found in 1 : 3-dithiolan (IV; $n = 2$) and 1 : 3-dithian (IV; $n = 3$). D. T. Gibson[36] has described the preparation of the former, by distilling a mixture of formaldehyde, sodium ethylene thiosulphate, and hydrochloric

[33] *Ber.*, 1925, **58**, [*B*], 1633; *A.*, 1925, i, 1307.

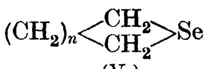
[34] *Ibid.*, 1930, **63**, [*B*], 313; *A.*, 612. [35] *J.*, 1927, 194. [36] *J.*, 1930, 12.

acid, and of the latter from trimethylene dibromide, sodium thiosulphate, formaldehyde, and hydrochloric acid.



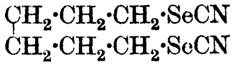
$(\mathrm{CH_2})_n\!<\!\begin{smallmatrix}\mathrm{S}\\ \mathrm{S}\end{smallmatrix}\!>\!\mathrm{CH_2}$

(IV.)



$(\mathrm{CH_2})_n\!<\!\begin{smallmatrix}\mathrm{CH_2}\\ \mathrm{CH_2}\end{smallmatrix}\!>\!\mathrm{Se}$

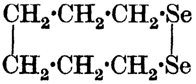
(V.)



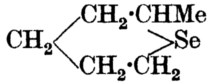
$\begin{array}{l}\mathrm{CH_2\cdot CH_2\cdot CH_2\cdot SeCN}\\ \mathrm{CH_2\cdot CH_2\cdot CH_2\cdot SeCN}\end{array}$

(VI.)

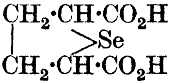
In addition to *cyclo*selenobutane and *cyclo*selenopentane, mentioned in last year's Report,[37] G. T. Morgan and F. H. Burstall[38] have now described the preparation of *cyclo*selenopropane (V; $n = 1$) and *cyclo*selenohexane (V; $n = 4$) in small yield by the interaction of sodium selenide with trimethylene dibromide and hexamethylene dibromide respectively. These substances are not only more difficult to prepare than their analogues, but they are also characterised by a greater degree of instability and a tendency to polymerise. In fact, the main product formed during the preparation of the former compound is a six-fold polymeride, and *cyclo*selenohexane also is accompanied by a dimeride and a complex polymeride. The new monomeric cyclic selenium compounds show the property, common to those previously described, of combining additively with such reagents as the halogens and mercuric chloride. By an extension of other reactions used in the earlier work, hexamethylene dibromide has been converted by the action of potassium selenocyanate into hexamethylene diselenocyanate (VI), which was transformed into *cyclo*hexamethylene 1 : 8-diselenide (VII) on treatment with alcoholic alkali. The latter decomposed, when heated, to give 2-methyl*cyclo*selenopentane (VIII).



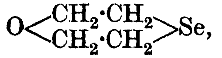
(VII.)



(VIII.)



(IX.)

A. Fredga[39] has prepared *cis*-tetrahydroselenophen-2 : 5-dicarboxylic acid (IX) by the action of potassium diselenide on sodium *meso*-αα′-dibromoadipate, and the corresponding *trans*-modification by the action of potassium selenide on sodium *dl*-αα′-dibromoadipate. The *trans*-form, as expected, was found to be resolvable by brucine. Also of interest is the preparation by C. S. Gibson and J. D. A. Johnson of 1 : 4-selenoxan,  $\mathrm{O}\!<\!\begin{smallmatrix}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{smallmatrix}\!>\!\mathrm{Se}$, by the action of sodium selenide on ββ′-dichlorodiethyl ether;[40] this substance, like those mentioned above, readily forms addition products.

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[37] *Ann. Reports*, 1929, **26**, 160.

[38] *J.*, 1930, 1497.

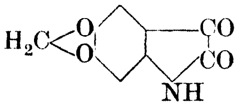
[39] *J. pr. Chem.*, 1930, [ii], **127**, 103; *A.*, 1196.

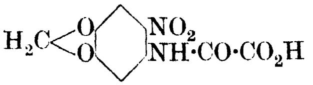
[40] *J.*, 1931, 266.

Indole Derivatives.

Some interesting observations in the isatin group have been recorded by J. M. Gulland, R. Robinson, J. Scott, and S. Thornley.[41] 5 : 6-Methylenedioxyisatin (I) undergoes ring fission, when treated with nitric acid, to give ox-6-nitro-3 : 4-methylenedioxyanilic acid (II). A similar reaction has been previously observed [42] between nitric acid and di(methylenedioxy)indigotin. A new route for the production of isatin derivatives is found in the prolonged hydrolysis, with boiling dilute aqueous-alcoholic sodium hydroxide, of the azlactone (III) derived from the interaction of 2-nitroveratraldehyde and hippuric acid. The formation of 6 : 7-dimethoxyisatin in this way provides another example of an interesting type of intramolecular oxidation–reduction.

(I.)

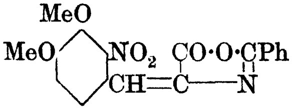


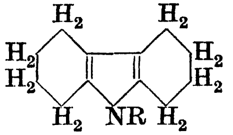


(II.)

S. G. P. Plant [43] has prepared 9-methyl- and 9-ethyl-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydrocarbazole (IV) by the action of the appropriate alkylamines on 2 : 2′-diketodi*cyclo*hexyl (V) in glacial acetic acid. These substances proved to be identical with compounds obtained by J. von Braun and H. Ritter [44] by the catalytic hydrogenation of the corresponding 9-alkylcarbazoles, and different from the alkylation products of the base obtained by the removal of ammonia from *cyclo*hexylideneazine [45] (VI). The last reaction, which is reminiscent of the preparation of tetraphenylpyrrole from phenyl benzyl ketazine,[46] does not, therefore, yield (IV; R = H), but an isomeric octahydrocarbazole, probably of the structure (VII).

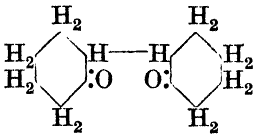
(III.)

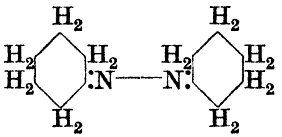




(IV.)

(V.)





(VI.)

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[41] *J.*, 1929, 2924. [42] T. G. Jones and R. Robinson, *J.*, 1917, **111**, 908.

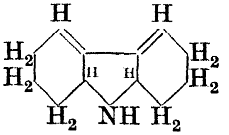
[43] *J.*, 1930, 1595. [44] *Ber.*, 1922, **55**, [*B*], 3792.

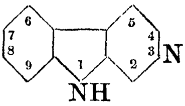
[45] W. H. Perkin and S. G. P. Plant, *J.*, 1924, **125**, 1503.

[46] (Mrs.) G. M. Robinson and R. Robinson, *J.*, 1918, **113**, 639.

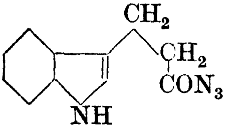
The system of nomenclature and numbering hitherto employed for the various carbolines has been anomalous and unsatisfactory. It has now been suggested,[47] in consequence, that 3-, 4-, 5-, and 6-carboline should be re-named α-, β-, γ-, and δ-carboline respectively, and that the accompanying numbering (formula VIII; β-carboline being used for illustration), which is more conventional, should be applied to all the four groups. In some recent papers these proposals have been adopted. The reaction previously observed by R. H. F. Manske and R. Robinson[48] in which the decomposition of the azide (IX) of β-3-indolylpropionic acid by hydrogen chloride in benzene is accompanied by intramolecular condensation with the formation of 2-keto-2 : 3 : 4 : 5-tetrahydro-β-carboline (X; R = H) has now been applied to the preparation of 2-keto-7-methoxy- and 2-keto-8-methoxy-tetrahydro-β-carboline.[49] The latter (X; R = MeO) was found to be identical with one of the substances obtained by the hydrolysis of the product of the oxidation (by permanganate) of acetylharmaline, and confirmation is consequently provided for the constitution (XI) assigned to acetylharmaline.[50]

(VII.)





(VIII.)



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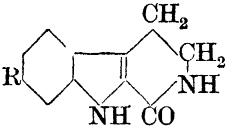
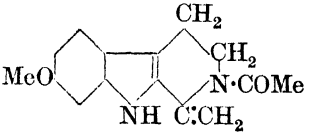


(X.)



(XI.)

Although the structures of harman, harmaline, and harmine have been already amply confirmed by synthesis,[51] additional methods developed by E. Späth and E. Lederer[52] are of interest, and are closely related to well-known reactions in the *iso*quinoline series. The acetyl derivative of 3-β-aminoethylindole has been converted by phosphoric oxide in boiling xylene into dihydroharman, which was subsequently dehydrogenated with spongy palladium at 200° to give harman (XII). A similar process applied to 6-methoxy-3-β-acetamidoethylindole led first to harmaline (XIII) and then to harmine (XIV). The same authors [53] have extended these reactions to other acyl derivatives of 3-β-aminoethylindole and certain of its substitution products for the purpose of preparing a large number of β-carbolines. They have also investigated the condensation of

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[47] J. M. Gulland, R. Robinson, J. Scott, and S. Thornley, *loc. cit.*

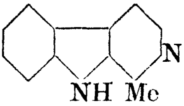
[48] *J.*, 1927, 240; *Ann. Reports*, 1927, **24**, 161.

[49] H. S. B. Barrett, (the late) W. H. Perkin, and R. Robinson, *J.*, 1929, 2942.

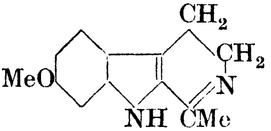
[50] H. Nishikawa, W. H. Perkin, and R. Robinson, *J.*, 1924, **125**, 657.

[51] See, *e.g.*, *Ann. Reports*, 1927, **24**, 160.

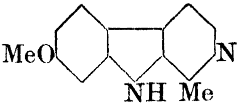
[52] *Ber.*, 1930, **63**, [*B*], 120; *A.*, 353.



(XII.)

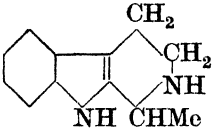


(XIII.)

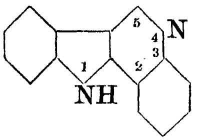


(XIV.)

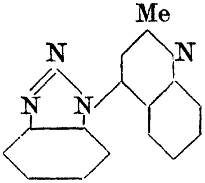
formaldehyde with some 3-β-aminoethylindoles, and the dehydrogenation of the resulting 2 : 3 : 4 : 5-tetrahydro-β-carbolines to β-carbolines by palladium at 160—170°. Further reactions of a similar type have been studied by S. Akabori and K. Saito.[54] Tetrahydroharman (XV) was prepared by the condensation of 3-β-aminoethylindole with acetaldehyde,[55] and was dehydrogenated to harman on being boiled in aqueous solution with maleic acid and palladium-black for five hours; an analogous procedure resulted in the conversion of 6-methoxy-3-β-aminoethylindole into harmine. This method of dehydrogenation, which involves the catalytic transference of hydrogen to an unsaturated compound, is of considerable interest, and has been applied by S. Akabori and his co-workers [56] to a number of other products, several different unsaturated substances being used.



(XV.)



(XVI.)



(XVII.)

By reactions analogous to those which have been used for the synthesis of γ-carboline,[57] W. O. Kermack and J. F. Smith [58] have obtained derivatives of 2 : 3-benz-γ-carboline (XVI). For example, 4-*o*-aminophenylamino-2-methylquinoline, from the interaction of 4-chloro-2-methylquinoline and *o*-phenylenediamine, was converted into a triazole derivative (XVII), which subsequently gave 5-methyl-

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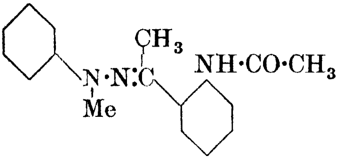
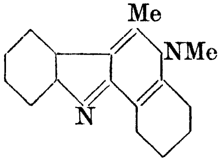
[53] *Ber.*, 1930, **63**, [*B*], 2102.
[54] *Ibid.*, p. 2245.
[55] Compare G. Tatsui, *J. Pharm. Soc. Japan*, 1928, **48**, 92.
[56] *Proc. Imp. Acad. Tokyo*, 1929, **5**, 256; 1930, **6**, 236; *A.*, 1929, 1170; 1930, 1192.
[57] R. Robinson and S. Thornley, *J.*, 1924, **125**, 2169.
[58] *J.*, 1930, 1999.

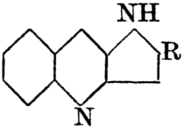
2 : 3-benz-γ-carboline by loss of nitrogen, on heating in syrupy phosphoric acid. The same authors have also prepared 1 : 5-dimethyl-2 : 3-benz-γ-carboline by treating *o*-acetamidoacetophenone phenylmethylhydrazone (XVIII) with phosphoryl chloride in boiling toluene. The methosulphate of this carboline is apparently identical with the methosulphate of the anhydronium base (XIX) derived from the action of alkali on the methosulphate of 5-methyl-2 : 3-benz-γ-carboline. This fact, together with the fluorescent properties of these carbolines, confirms the structures assigned to them. The anhydronium base (XIX) is analogous to the anhydronium bases derived from certain β-carbolines,[59] and its preparation has an added interest in view of the behaviour of other closely related substances. Thus (Mrs.) G. M. Robinson[60] has prepared 2 : 3-pyrrolo(4′ : 5′)-quinolines (XX) by the dehydration of 3-acylamidoquinaldines (XXI), an extension of a reaction previously used in the pyrindole series,[61] and has found that the methosulphate of 2 : 3-(2′-phenylpyrrolo)(4′ : 5′)-quinoline (XX; R = Ph) readily yields an anhydronium base (XXII) with aqueous sodium hydroxide. It has been noted, however, that quindoline methosulphate (XXIII) gives no analogous anhydronium base.[62]



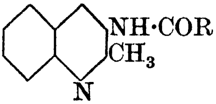
(XVIII.)



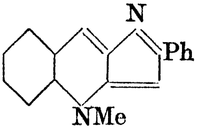
(XIX.)



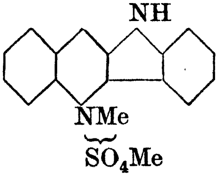
(XX.)



(XXI.)

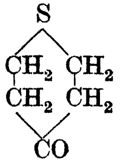


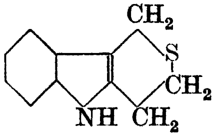
(XXII.)



(XXIII.)

Mention may be made in this section of an interesting application of Fischer's indole synthesis to the phenylhydrazone of penthian-

(XXIV.)




(XXV.)

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[59] See *Ann. Reports*, 1928, **25**, 176.

[60] *J.*, 1929, 2948.

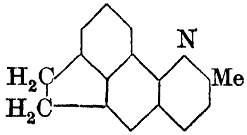
[61] E. Koenigs and A. Fulde, *Ber.*, 1927, **60**, [*B*], 2106.

[62] J. W. Armit and R. Robinson, *J.*, 1922, **121**, 827.

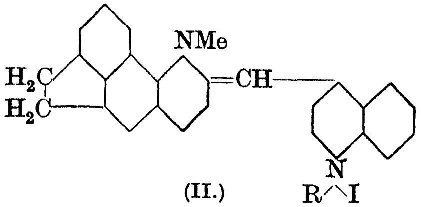
4-one (XXIV), which resulted in the formation of penthienoindole[63] (XXV).

Quinoline Derivatives.

Further interesting developments in the chemistry of the cyanine dyes have recently been recorded. With a view to the study of some physical properties, Miss F. M. Hamer[64] has investigated the possibility of preparing examples of known classes of these dyes from certain more complex compounds of the quinaldine or lepidine type, containing a reactive methyl group. From the interaction of the methiodide of 2-methylacenaphthpyridine (I) and the quinoline alkyliodides, *iso*cyanines of the formula (II) resulted, and, with the 2-iodoquinoline alkyliodides, ψ-cyanines of the constitution (III) were obtained by the usual methods, but attempts to prepare a carbocyanine from it by the well-known procedure with ethyl orthoformate and pyridine were unsuccessful. Although 5-methylacridine (IV) contains a reactive methyl group, attempts to prepare a carbocyanine from its methiodide or to effect condensation with quinoline methiodide by the usual methods met with failure. However, from the condensation of 5-methylacridine methiodide with 2-iodoquinoline alkyliodides in aqueous potassium hydroxide dyes were obtained to which the formula (V) has been attributed, but their physical properties were somewhat abnormal.

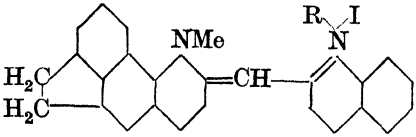


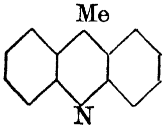
(I.)



(II.)

(III.)





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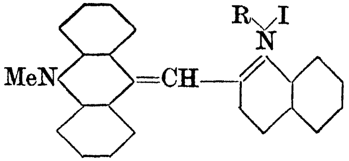
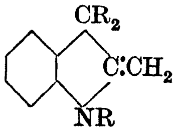


(V.)



(VI.)

An interesting and surprising new route for the production of thiocyanines, which in several respects is superior to the older methods, has been discovered by Miss N. I. Fisher and Miss F. M. Hamer.[65] The process came to light during an attempt to apply the reaction by which 2-methylene-1 : 3 : 3-trialkylindolines (VI), or the corresponding indoleninium salts (VII), are converted into dyes of the type (VIII; $A = CR_2$)[66] to the preparation of the corresponding sulphur compounds (VIII; A = S). The action of amyl nitrite, in the presence of acetic anhydride, on the alkylchlorides of 1-methylbenzthiazole (IX) led unexpectedly to the thiocyanines (X). The course of this reaction is not obvious, although the authors have put forward tentative suggestions. It is well known that it is very difficult to prepare cyanine and carbocyanine dyes from monocyclic compounds, although certain carbopyridinecyanines have recently been prepared.[67] It is not surprising, therefore, that the new method for the preparation of thiocyanines fails when applied to the alkylchlorides of 2 : 4-dimethylthiazole (XI). Our knowledge of the simpler types has, however, been extended by these authors by the preparation of thiocarbocyanines of the formula (XII) from the action of ethyl orthoformate and pyridine on the 2 : 4-dimethylthiazole alkyliodides.

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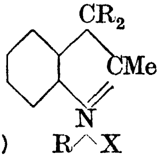
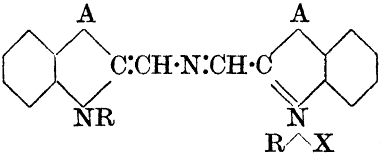
[63] G. M. Bennett and W. B. Waddington, *J.*, 1929, 2829. [64] *J.*, 1930, 995.

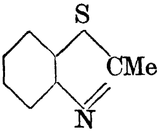
(VII.)

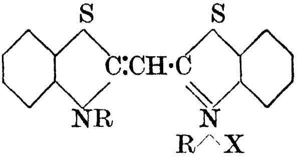




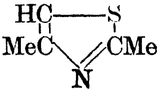
(VIII.)

(IX.)

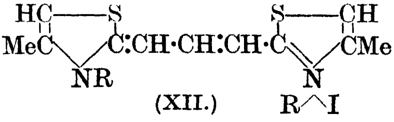




(X.)



(XI.)



(XII.)

Some interesting observations have been made by G. R. Clemo and H. J. Johnson[68] during the course of experiments designed for the purpose of synthesising 12 : 13-dimethoxy*iso*indenoquinoline (XIII*a* and XIII*b*). The condensation of 4-keto-1 : 2 : 3 : 4-tetrahydroquinoline with veratraldehyde in alcoholic sodium hydroxide led to 4-hydroxy-3-veratrylquinoline (XIV), but the various alternative routes which were explored in order to effect conversion

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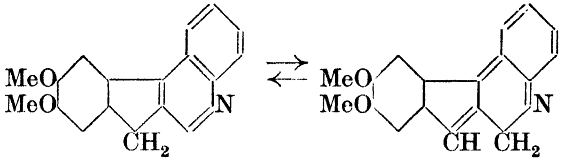
[65] *J.*, 1930, 2502.

[66] D.R.-P. 459, 616; B.P. 291, 888.

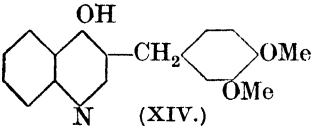
[67] See *Ann. Reports*, 1929, **26**, 164.

[68] *J.*, 1930, 2133.

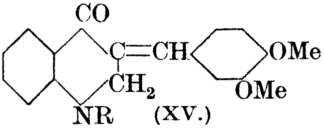


(XIIIa.) (XIIIb.)

of this product into (XIII) failed to give the desired result. It was found, however, that, when these two substances were condensed in glacial acetic acid in the presence of hydrogen chloride, the reaction yielded 4-keto-3-veratrylidene-1 : 2 : 3 : 4-tetrahydroquinoline (XV; R = H), which was easily transformed into (XIV) by the action of

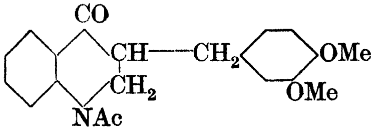


(XIV.)

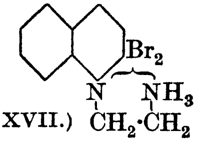


(XV.)

alcoholic alkali. By the use of 4-keto-1-acetyl-1 : 2 : 3 : 4-tetrahydroquinoline this latter possibility was avoided and the product (XV; R = Ac) then gave 4-keto-1-acetyl-3-veratryl-1 : 2 : 3 : 4-tetrahydroquinoline (XVI) on catalytic reduction. The substance (XVI) was converted into (XIII) by the action of warm sulphuric acid (80%), a process which involved deacetylation and oxidation in addition to ring closure. The product was obtained in two interconvertible forms (one faintly yellow and the other reddish-brown) which apparently are represented by the structures (XIIIa) and (XIIIb) respectively.



(XVI.)



(XVII.)

T. R. Seshadri,[69] during an investigation of some aminoalkylquinolinium salts, has made the interesting observation that the action of aqueous sodium hydroxide on β-aminoethylquinolinium bromide hydrobromide (XVII) leads to a base for which the structure (XVIII) is proposed. S. Gabriel [70] suggested the constitution (XIX) for an analogous pyridine derivative, but this is very unlikely.

Investigations by S. G. P. Plant and R. J. Rosser [71] into the reduction of certain simple quinolines under various conditions have shown that, although 2 : 3-dimethyl- and 2 : 4-dimethylquinoline readily give the two stereoisomeric modifications (*cis-* and *trans-*) of 2 : 3-dimethyl- and 2 : 4-dimethyl-1 : 2 : 3 : 4-tetrahydroquinoline respectively, the 3 : 4-dimethyl compound yields only one of the two possible forms of its tetrahydro-derivative. An explanation of this fact can be found in the steric effect of the 4-methyl group in the intermediate 3 : 4-dimethyl-1 : 4-dihydroquinoline, which is to displace the 3-methyl group from its symmetrical position with respect to the double bond. As a result of this, the subsequent addition of a hydrogen atom in the 3-position takes place in one only of the two possible directions. The action of sodium amalgam upon 2-keto-3 : 4-dimethyl-1 : 2-dihydroquinoline in alcoholic solution led to the two forms of (XX), but further reduction of this mixture by sodium and alcohol resulted in the single modification of 3 : 4-dimethyl-1 : 2 : 3 : 4-tetrahydroquinoline. This fact is almost certainly explained by the intermediate formation in the latter reaction of 3 : 4-dimethylquinoline, traces of which were found in the product. A similar explanation will account for the formation of only one modification of 2 : 3 : 4 : 5 : 6 : 13-hexahydro-α-quinindene (XXI) during the reduction of a mixture of the two stereoisomeric forms of 5-keto-2 : 3 : 4 : 5 : 6 : 13-hexahydro-α-quinindene [72] (XXII).

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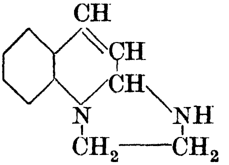
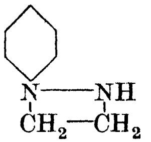
[69] *J.*, 1929, 2952.

[70] *Ber.*, 1920, **53**, [*B*], 1985.

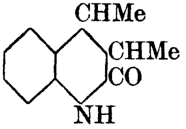
[71] *J.*, 1929, 1861; 1930, 2444.



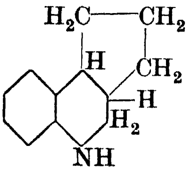
(XVIII.)



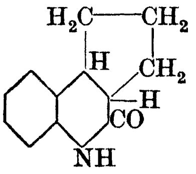
(XIX.)



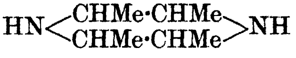
(XX.)



(XXI.)



(XXII.)


$HN<\begin{smallmatrix}CHMe\cdot CHMe\\CHMe\cdot CHMe\end{smallmatrix}>NH$

(XXIII.)

Five geometrical isomerides are possible in the case of 2 : 3 : 5 : 6-tetramethylpiperazine (XXIII), and it is of interest to record that F. B. Kipping [73] has isolated four of these by reducing 2 : 3 : 5 : 6-

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[72] B. K. Blount, W. H. Perkin, and S. G. P. Plant, *J.*, 1929, 1975; *Ann. Reports*, 1929, **26**, 164.

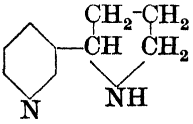
[73] *J.*, 1929, 2889.

tetramethylpyrazine under various conditions. Previously only two had been definitely identified.

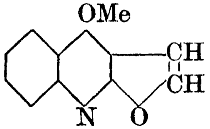
Alkaloids.

In a study of the de-alkylation of tertiary amines by heating with organic acids J. von Braun and K. Weissbach [74] have included an investigation of some cyclic bases. 2-Methyltetrahydro*iso*quinoline was converted into 2-benzoyl- and 2-β-phenylpropionyltetrahydro*iso*quinoline by the action of the appropriate acid, and tropane yielded benzoyl- and β-phenylpropionyl-nortropane under similar conditions. Nicotine, on like treatment, gave products containing acylnornicotines, from which nornicotine (I) was obtained on hydrolysis.

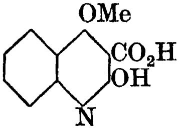
Quinoline Group.—Further investigations by E. Späth and J. Pikl [75] into the nature of the products obtained from angostura bark have resulted in the separation of four additional bases from the low-boiling fraction, *viz.*, quinoline, 2-methylquinoline, 2-keto-1-methyl-1 : 2-dihydroquinoline, and 2-*n*-amylquinoline. The isolation of such simple bases from this source is of considerable interest.



(I.)



(II.)



(III.)

Y. Asahina, T. Ohta, and M. Inubuse [76] have isolated from *Skimmia repens* a base, $C_{12}H_9O_2N$, which was found to be identical with dictamnine, an alkaloid obtained from *Dictamnus albus*,[77] and, from a study of its reactions, the formula (II) has been suggested. Thus it was found to contain one methoxyl group, the second oxygen atom appeared to be of the ether type, and, on oxidation with potassium permanganate, the alkaloid gave an aldehyde (dictamnal), $C_{11}H_9O_3N$, together with the corresponding acid (dictamnic acid), $C_{11}H_9O_4N$. The latter, on heating with concentrated hydrochloric or hydrobromic acid, yielded 2 : 4-dihydroxyquinoline with the loss of a methyl group and carbon dioxide; it was found, however, not to be identical with a synthetical specimen of 4-hydroxy-2-methoxyquinoline-3-carboxylic acid,[78] so that it appears to be 2-hydroxy-4-methoxyquinoline-3-carboxylic acid (III).

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[74] *Ber.*, 1930, **63**, [*B*], 489, 2018; *A.*, 458, 1444.

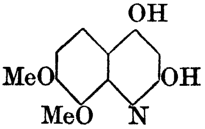
[75] *Monatsh.*, 1930, **55**, 352; *A.*, 1049; for earlier work, see *Ann. Reports*, 1924, **21**, 131; 1929, **26**, 170.

[76] *Ber.*, 1930, **63**, [*B*], 2045; *A.*, 1454.

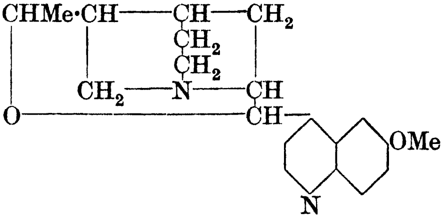
[77] H. Thoms, *A.*, 1923, i, 639.

[78] Prepared by a method analogous to that described by C. A. Bischoff, *Annalen*, 1889, **251**, 360.

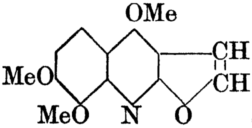
It has also been shown, by Y. Asahina and M. Inubuse,[79] that the alkaloid skimmianine, isolated by J. Honda [80] from *Skimmia japonica,* has the molecular formula $C_{14}H_{13}O_4N$ and is closely related to dictamnine. It contains three methoxyl groups, and, on oxidation with potassium permanganate, it yielded an aldehyde, $C_{13}H_{13}O_5N$, and an acid, $C_{13}H_{13}O_6N$. The acid, on heating with concentrated hydrochloric acid, lost a methyl group and carbon dioxide with the formation of a product which was shown synthetically to be 2 : 4-dihydroxy-7 : 8-dimethoxyquinoline (IV).



(IV.)



(VI.)



(V.)

This synthesis was accomplished [81] by condensing 2-nitro-3 : 4-dimethoxybenzoyl chloride with malonic ester and heating the product with tin and alcoholic hydrochloric acid. Skimmianine, therefore, appears to be a dimethoxydictamnine of the constitution (V).

*iso*Quinidine, which does not occur naturally, is obtained when its isomeride, quinidine (itself a naturally occurring isomeride of quinine), is dissolved in warm sulphuric acid. A. Konopnicki and J. Suszko [82] assert that several of the reactions of *iso*quinidine are explicable with the aid of formula (VI). It is not acted upon by acid chlorides, acetic anhydride, the Grignard reagent, phenylhydrazine, or semicarbazide. The base also forms a mono- and a di-methiodide, an oxide (with hydrogen peroxide), and two perbromides, both of which give *iso*quinidine with dilute alkalis. By heating *iso*quinidine sulphate alone, or the free base in 25% acetic acid, another isomeride, *iso*quinicine, is produced. The latter is not ketonic in character, but appears to contain an >NH group, which can be acetylated, nitrosated, and methylated.

iso*Quinoline Group.*—A considerable amount of work dealing with the chemistry of substances of the papaverine type has been recorded during the year. By suitable modification of the well-known synthesis of Pictet and Gams,[83] J. S. Buck [84] has prepared the hitherto unknown 1 : 2-dihydropapaverine (IV). ω-Homoveratroylaminoacetoveratrone (I) was dehydrated by means of phosphoryl chloride to give (II); this was catalytically reduced to (III), which was treated with phosphorus pentachloride in cold

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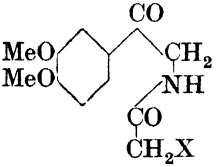
[79] *Ber.*, 1930, **63**, [*B*], 2052; *A.*, 1454.

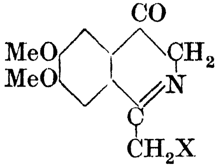
[80] *A.*, 1905, i, 152.

[81] Y. Asahina and S. Nakanishi, *Ber.*, 1930, **63**, [*B*], 2057; *A.*, 1445.

[82] *Bull. Acad. Polonaise*, 1929, *A*, 340; *A.*, 1930, 97.



(I.)



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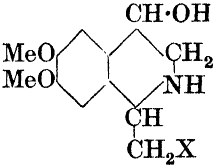
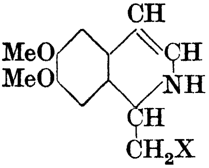


(III.)



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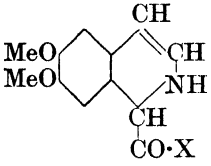

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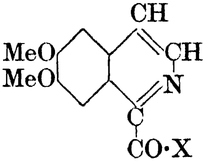


(VI.)

(X = 3 : 4-dimethoxyphenyl)

chloroform with the production of (IV). 1 : 2-Dihydropapaverine was reduced catalytically to tetrahydropapaverine, and dehydrogenated to give papaverine by heating with palladium-black. It readily underwent oxidation by air to the ketone (V), and, when heated with methyl-alcoholic potassium hydroxide, it yielded papaveraldine (VI). In the latter reactions 1 : 2-dihydropapaverine closely resembles its 3 : 4-isomeride.[85]

I. Allen and J. S. Buck [86] have investigated the possibility of preparing substances of the papaverine type by the application of a reaction already used in the *iso*quinoline series,[87] *viz.*, from derivatives of benzylaminoacetal by ring closure and oxidation. The oxime of deoxyveratroin (VII) was reduced with sodium amalgam and alcoholic acetic acid to αβ-di-(3 : 4-dimethoxyphenyl)-ethylamine (VIII), but the product derived from the condensation of this substance and bromoacetal was completely decomposed by treatment with sulphuric acid and arsenic oxide in an attempt to prepare papaverine. Similar results were obtained with the analogous di-methylenedioxy-derivative from deoxypiperoin.

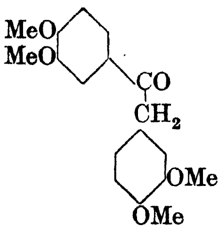
[83] *Ber.*, 1909, **42**, 2943.

[84] *J. Amer. Chem. Soc.*, 1930, **52**, 3610; *A.*, 1455.

[85] See J. S. Buck, R. D. Haworth, and W. H. Perkin, *J.*, 1924, **125**, 2176.

[86] *J. Amer. Chem. Soc.*, 1930, **52**, 310; *A.*, 353.

[87] See, *e.g.*, L. Rügheimer and P. Schön, *Ber.*, 1909, **42**, 2374.



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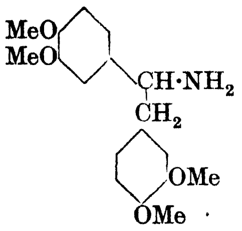

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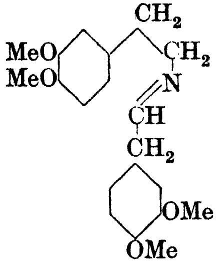
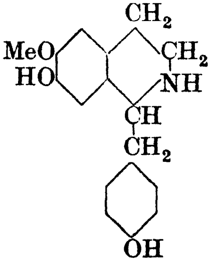


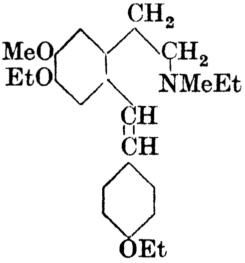
(IX.)

Having in mind the possible route by which the papaverine alkaloids are formed in nature,[88] E. Späth and F. Berger [89] have studied the condensation of homoveratrylamine with 3 : 4-dimethoxyphenylacetaldehyde, and the conversion of the product (IX) into *dl*-tetrahydropapaverine. Ring closure was accomplished with 19% hydrochloric acid, but the yield of the tetrahydro-base was small (8%).

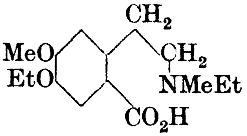
An investigation by H. Kondo and T. Kondo [90] of the reactions of coclaurine, an alkaloid from *Cocculus laurifolius*, has shown that it is represented by the formula (X). The following were the main observations which led to this result and established the relative positions of the methoxyl and hydroxyl groups. The methosulphate of the triethyl derivative of coclaurine gave a product (XI) by the Hofmann degradation process, which, on oxidation, yielded *p*-ethoxybenzoic acid and the acid (XII). The structure of the latter was established by a further application of the Hofmann process to give 4-methoxy-3-ethoxy-6-vinylbenzoic acid, and, on subsequent reduction, 4-methoxy-3-ethoxy-6-ethylbenzoic acid, the identity of which was confirmed by synthesis. Furthermore, the dehydration of *p*-methoxyphenylaceto-β-3 : 4-dimethoxyphenyl-



(X.)



(XI.)



(XII.)

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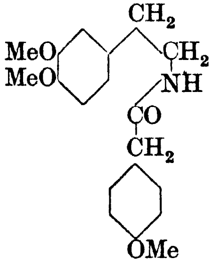
[88] See R. Robinson, *J.*, 1917, **111**, 876.

[89] *Ber.*, 1930, **63**, [*B*], 2098; *A.*, 1454.

[90] *J. pr. Chem.*, 1930, [ii], **126**, 24; *A.*, 794.

ethylamide (XIII) gave an *iso*quinoline derivative, which, on reduction and subsequent treatment with methyl sulphate, gave the methosulphate of trimethylcoclaurine; the latter was identical with the product obtained directly from the alkaloid by the action of methyl sulphate and alkali. The formula (XIV) has been assigned



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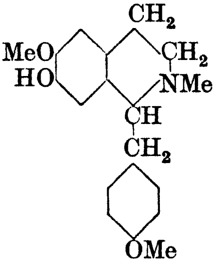

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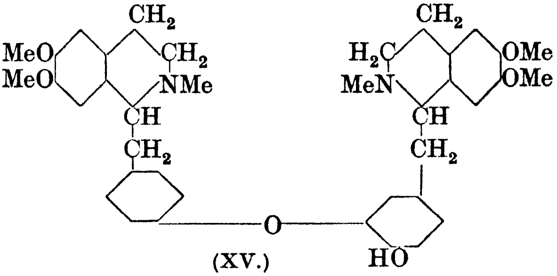

(XV.)

by H. Kondo and Z. Narita [91] to dauricine, an alkaloid from *Menispermum dauricum,* as a result of an investigation of the oxidation products derived from the nitrogen-free compounds obtained by an application of the Hofmann degradation process to methyldauricine methiodide and ethyldauricine ethobromide. The alkaloid thus appears to be closely related to coclaurine, although F. Faltis and H. Frauendorfer [92] have expressed the view that it has a more complex structure (XV) of the bimolecular type with an oxygen bridge.

In the formulæ previously advanced for *iso*chondodendrine methyl ether [93] the exact points of attachment of the two methoxyl groups and the ether-oxygen to the *iso*quinoline system have been in doubt. In solving this particular problem much has depended upon the positions of the substituent groups in a tricarboxydimethoxydiphenyl ether which was obtained by the oxidation of the product derived from the Hofmann degradation of the methyl ether. F. Faltis and H. Frauendorfer [94] have now established synthetically that this acid is 2 : 3-dimethoxydiphenyl ether 5 : 6 : 4′-tricarboxylic acid (XVI), a fact which necessitates a revision of the earlier formulæ in favour of one of the two alternatives (XVII) and (XVIII).

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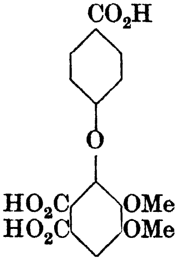
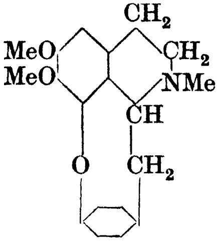
[91] *Chem. Zentr.*, 1927, ii, 264; 1929, ii, 1926; *Ber.*, 1930, **63**, [*B*], 2420.

[92] *Ber.*, 1930, **63**, [*B*], 806. [93] See *Ann. Reports*, 1928, **25**, 190. [94] *Loc. cit.*



(XVI.)



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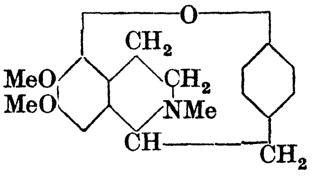
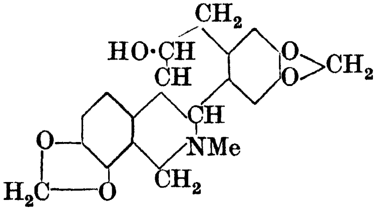


(XVIII.)

The formulæ previously assigned to chelidonine cannot be regarded as satisfactory, and, as a result of a review of the reactions of this alkaloid, together with a consideration of its relationship to protopine and a re-investigation of the structure of a degradation product, F. von Bruchhausen and H. W. Bersch[95] have now advanced the formula (XIX). Confirmation of these views from degradative and synthetical experiments will be awaited with interest, since the structures to be assigned to related alkaloids, such as chelerythrine, are involved.



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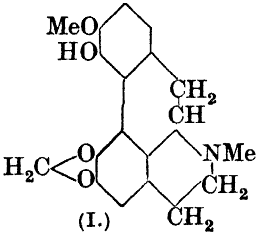

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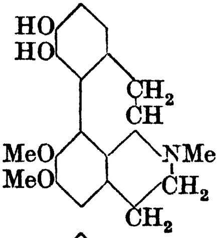

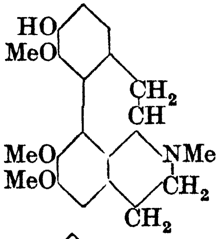

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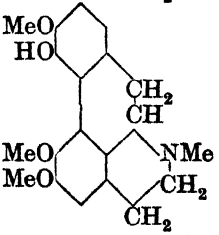

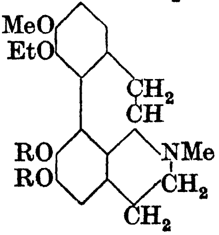

(V.)

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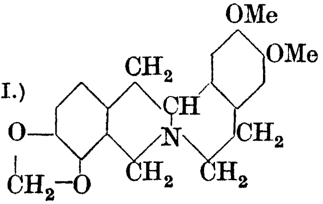
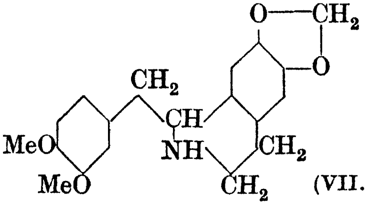
[95] *Ber.*, 1930, **63**, [*B*], 2520.

Aporphine Group.—After considerable activity during the preceding two years, there is comparatively little to record on this occasion concerning members of the aporphine group. One interesting development, however, has been the isolation and investigation by J. Go[96] of *l*-corydine and *d*-*iso*corydine, together with other alkaloids, from *Corydalis ternata.* Previous work[97] has settled the structures of the closely related alkaloids bulbocapnine (I) and corytuberine (II), and J. Gadamer[98] has suggested the formulæ (III) and (IV) for corydine and *iso*corydine respectively, a mixture of these two products being obtained by the monomethylation of corytuberine. The new work indicates, however, that corydine has the structure (IV) and *iso*corydine (III). Thus bulbocapnine ethyl ether was converted into the substance (V; R = H) and subsequently methylated, the resulting derivative (V; R = Me) being found to be identical with *d*-corydine ethyl ether.

Diïsoquinoline Group.—K. Goto and H. Sudzuki[99] recently described the isolation of a new alkaloid, sinactine, in small quantities from *Sinomenium acutum,* and it has now been identified by K. Goto and Z. Kitasato[1] as *l*-tetrahydro*epi*berberine (VI). Oxidation with iodine in alcoholic solution led to *epi*berberinium salts, which, on subsequent reduction of the chloride, yielded *dl*-sinactine; this proved to be identical with a specimen of synthetical *dl*-tetrahydro*epi*berberine.[2]

(VI.)





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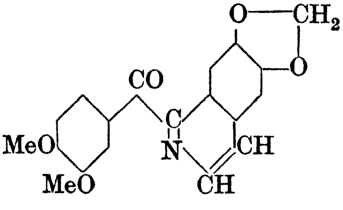

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[96] *J. Pharm. Soc. Japan,* 1929, **49,** 125, 126, 129; *Chem. Zentr.,* 1930, i, 234.

[97] See *Ann. Reports,* 1928, **25,** 187.

[98] *Arch. Pharm.,* 1911, **249,** 503.

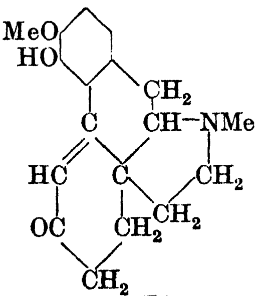
[99] *Bull. Chem. Soc. Japan,* 1929, **4,** 220; *Ann. Reports,* 1929, **26,** 181.

[1] *J.,* 1930, 1234.

[2] W. H. Perkin, *J.,* 1918, **113,** 512; R. D. Haworth and W. H. Perkin, *J.,* 1926, 1777.

The supposed synthesis of tetrahydroberberine by Pictet and Gams[3] was shown to be unsound by the work of R. D. Haworth, W. H. Perkin, and J. Rankin,[4] and further investigations of the reactions concerned have now been described by J. S. Buck and R. M. Davis,[5] who have shown that the substance which was believed by Pictet and Gams to be veratrylnorhydrohydrastinine (VII) is, in reality, 9-keto-6 : 7-methylenedioxy-3′ : 4′-dimethoxyprotopapaverine (VIII). In actual fact, a mixture of these two products was found to result during the earlier stages of the synthesis.

Morphine Group.—The " thebainone " prepared by R. Pschorr[6] by reducing thebaine with stannous chloride and concentrated hydrochloric acid is regarded by C. Schöpf and F. Borkowsky[7] as having the structure (I). Since dihydrothebainone, hydroxythebainone, and hydroxydihydrothebainone do not have the same ring system as Pschorr's product, it is now suggested by C. Schöpf and (Frl.) H. Perrey[8] that the latter should be called " metathebainone," the name " thebainone " being reserved for the substance (II).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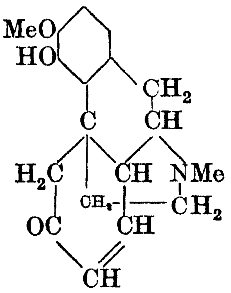
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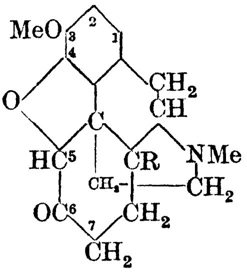

(III.)

The conversion of derivatives of dihydrocodeinone (III; R = H) into compounds of the dihydrothebainone (IV; R = H) type, with the rupture of the oxygen bridge and consequent appearance of a phenolic hydroxyl group in the 4-position, is well known as a feature of hydrogenation processes in the morphine series. The converse transformation of dihydrothebainone into dihydrocodeinone has now been accomplished by C. Schöpf and T. Pfeifer[9] by first converting the former substance into its 1-bromo-derivative. Further bromination gave a product (V), which, by treatment with alkali,

[3] *Ber.*, 1911, **44**, 2480.

[4] *J.*, 1924, **125**, 1686; *Ann. Reports*, 1924, **21**, 134.

[5] *J. Amer. Chem. Soc.*, 1930, **52**, 660; *A.*, 485.

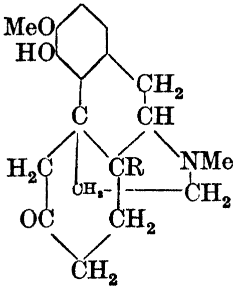
[6] *Ber.*, 1905, **38**, 3160.

[7] *Annalen*, 1927, **458**, 148; *Ann. Reports*, 1928, **25**, 192.

[8] *Annalen*, 1930, **483**, 169.

[9] *Ibid.*, p. 157.

yielded 1-bromodihydrocodeinone. The removal of the halogen atom with the formation of dihydrocodeinone was accomplished by catalytic hydrogenation. The reduction of 1-bromodihydrocodeinone with zinc dust in alcohol gave 1-bromodihydrothebainone. By a similar series of reactions hydroxydihydrothebainone (IV; R = OH) has been converted into hydroxydihydrocodeinone (III; R = OH), and the bromosinomeneine obtained by the successive action of bromine and alkali on sinomenine[10] (VI) is apparently formed by an analogous process and can be represented by the formula (VII), whereby it appears as an optical isomeride of 1-bromo-7-methoxycodeinone. By bromination of dihydrometathebainone (VIII) (previously called " thebainol "), followed by the action of alkali, 1-bromodihydrometacodeinone has been obtained, and this has been converted by catalytic hydrogenation into dihydrometacodeinone[11] (IX), which can be transformed into dihydrometathebainone again by the action of sodium amalgam. Dihydrometacodeinone is readily converted by acids or alkalis into the isomeric metathebainone (I).



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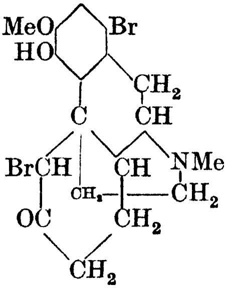

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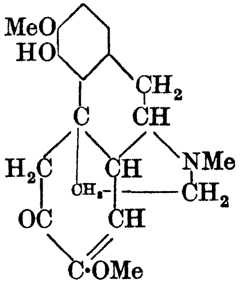

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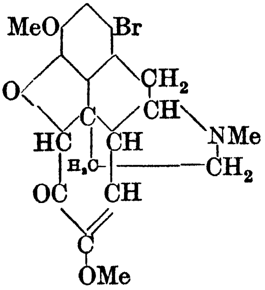

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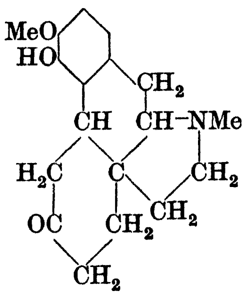

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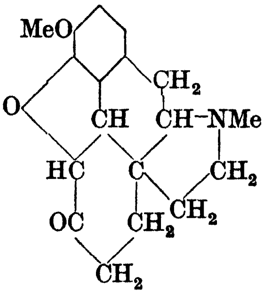

(IX.)

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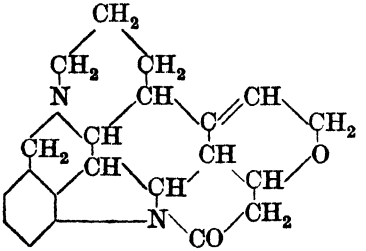
[10] K. Goto, *J. Chem. Soc. Japan*, 1923, **44**, 815; K. Goto and T. Nakamura, *Bull. Chem. Soc. Japan*, 1929, **4**, 195; K. Goto and T. Nambo, *ibid.*, 1930, **5**, 165.

[11] C. Schöpf and (Frl.) H. Perrey, *loc. cit.*

The spatial configurations of several members of the morphine group have recently been discussed by H. Emde.[12]

Strychnine.—Further investigations into the chemistry of strychnine derivatives have necessitated the abandonment of formula (I), which was advanced for this alkaloid two years ago,[13] and, in its place, a new formula (II) has been put forward by K. N. Menon, (the late) W. H. Perkin, and R. Robinson.[14] In the development of these structural views much has depended on the nature of dinitrostrycholcarboxylic acid, $C_9NH_2(OH)_2(NO_2)_2{\cdot}CO_2H$, which is obtained from the alkaloid by heating it first with dilute and then with concentrated nitric acid. A fundamental postulate in the development of the earlier structure was that dinitrostrychol is a dinitrodihydroxy*iso*quinoline, but it has now been conclusively shown that this substance is a quinoline derivative, as originally believed. Thus dinitrostrycholcarboxylic acid was converted during esterification into ethyl dinitro-*O*-ethylstrycholcarboxylate, $C_9NH_2(NO_2)_2(OH)(OEt){\cdot}CO_2Et$, which was transformed *via* the hydrazide and the usual Curtius reactions into the corresponding urethane, $C_9NH_2(NO_2)_2(OH)(OEt){\cdot}NH{\cdot}CO_2Et$. The urethane, unlike dinitrostrycholcarboxylic acid, was degraded by hot nitric acid to yield picric acid, a result which is consistent with a quinoline, but not an *iso*quinoline, structure for strychol. Furthermore, the urethane, by hydrolysis and subsequent oxidation with permanganate, was converted into 5 : 7-dinitroisatin (III). From the evidence



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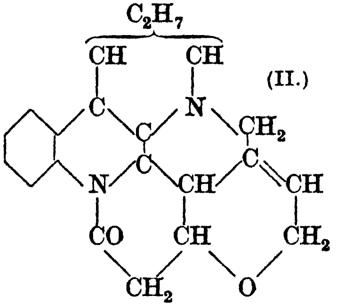

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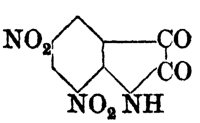

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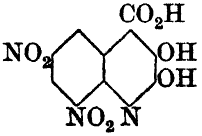

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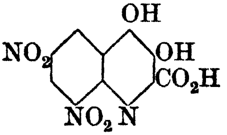

(V.)

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[12] *Helv. Chim. Acta*, 1930, **13**, 1035.

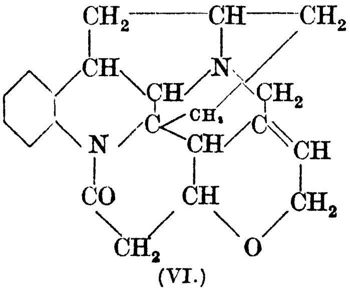
[13] R. C. Fawcett, W. H. Perkin, and R. Robinson, *J.*, 1928, 3082; W. H. Perkin and R. Robinson, *J.*, 1929, 964; *Ann. Reports*, 1928, **25**, 193; 1929, **26**, 181.

[14] *J.*, 1930, 830.

now available it is possible to say that dinitrostrycholcarboxylic acid must have one of the structures (IV) and (V).

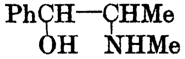
It will be noticed that the carbazole nucleus, a feature of formula (I) as well as of the original strychnine formula of W. H. Perkin and R. Robinson,[15] is absent from the new structure. The evidence for its presence, *viz.*, the isolation of carbazole from the degradation of the strychnine molecule, was always uncertain on account of the vigorous nature of the experimental conditions and the ease with which the carbazole system can be formed from other types. Several characteristics of formula (I) must, however, be regarded as established, *e.g.*, the existence and arrangement of the ether oxygen and the ethylenic linkage, and these are embodied in the new formula.

A fundamental point in the development of formula (II) is that the hydroxyl group in position 3 in the quinoline ring of dinitrostrycholcarboxylic acid fixes the position of the second nitrogen atom in strychnine. Only in this way can the formation of the 3-hydroxyl group during the degradation of strychnine be accounted for. The new formula provides an excellent explanation of many of the complex changes observed in the chemistry of this alkaloid and thereby obtains further justification. Thus, for example, the presence of the grouping $:N\cdot CH_2\cdot C:CH\cdot CH_2\cdot O\cdot$, and its successive transformation to $:N\cdot CO\cdot C(OH)\cdot CO\cdot CH_2\cdot O\cdot$, $:N\cdot CO\cdot CH(OH) + CO_2H\cdot CH_2\cdot O\cdot$ (by hydrolysis), and $:N\cdot CO\cdot CO + CO_2H\cdot CH_2\cdot O\cdot$, accounts for the formation of dihydrostrychninonic acid, and then strychninonic acid, by the oxidation of strychnine with permanganate. In formula (II) the exact arrangement of certain carbon and hydrogen atoms, comprising C_2H_7, still remains to be decided. There are several possibilities, and the authors suggest provisionally a bridge formulation of the type (VI), which is closely related to the cinchonine structure.



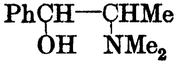
(VI.)

Miscellaneous Alkaloids.—Of the many possible stereoisomeric modifications of ephedrine and related substances, six have so far been recognised amongst the constituents of the Chinese drug Ma Huang, *viz.*, *l*-ephedrine (I), *d*-ψ-ephedrine (I), *l*-methylephedrine (II), *d*-methyl-ψ-ephedrine (II), nor-*d*-ψ-ephedrine (III), and nor-



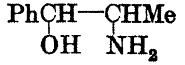
$PhCH(OH)-CH(NHMe)Me$

(I.)



$PhCH(OH)-CH(NMe_2)Me$

(II.)



$PhCH(OH)-CH(NH_2)Me$

(III.)

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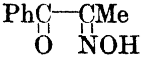
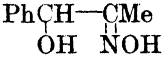
[15] *J.*, 1910, **97**, 305.

l-ephedrine (III).[16] Considerable work has recently been devoted to the synthesis of the two stereoisomeric inactive bases, nor-*dl*-ephedrine and nor-*dl*-ψ-ephedrine, of the formula (III). D. H. Hey[17] has found that the direct reduction of *iso*nitrosopropiophenone (IV) in the desired direction is difficult, although it has apparently been achieved catalytically,[18] but the action of sodium amalgam on phenylacetylcarbinol oxime (V) in dilute acetic acid solution led more readily to a mixture of the two stereoisomerides. In addition, W. N. Nagai and S. Kanao[19] found that the reduction of β-nitro-α-phenylpropyl alcohol (VI) with iron and aqueous alcoholic sulphuric acid, or with tin and hydrochloric acid, led to a mixture of the two inactive bases (III), which were subsequently resolved with the aid of *d*- and *l*-tartaric acids. C. S. Gibson and B. Levin[20] have employed the natural nor-*d*-ψ-ephedrine as a convenient base for the resolution of some externally compensated acids.



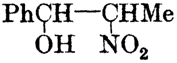
$\underset{\underset{\mathrm{O}}{\|}}{\mathrm{PhC}}-\underset{\underset{\mathrm{NOH}}{\|}}{\mathrm{CMe}}$

(IV.)



$\underset{\underset{\mathrm{OH}}{|}}{\mathrm{PhCH}}-\underset{\underset{\mathrm{NOH}}{\|}}{\mathrm{CMe}}$

(V.)



$\underset{\underset{\mathrm{OH}}{|}}{\mathrm{PhCH}}-\underset{\underset{\mathrm{NO_2}}{|}}{\mathrm{CHMe}}$

(VI.)

Previous investigations into the alkaloids of ergot have shown that ergotoxine and ergotinine are interconvertible, as also are ergotamine and ergotaminine. Furthermore, the properties and pharmacological action of ergotoxine and ergotamine hitherto described are so similar as to have promoted suspicion that these two alkaloids are really identical and that small observed differences were due to impurities. This possibility has now been removed by S. Smith and G. M. Timmis,[21] who have prepared all four alkaloids in a state of purity from different specimens of ergot. A careful examination of their physical properties clearly indicates that they are definite and distinct substances. Little evidence is, as yet, forthcoming regarding the constitutions and inter-relationships of these alkaloids.

Mention may be made in this section of interesting developments which have recently occurred in the chemistry of certain pungent acid amides. The structure (VII; R = H) assigned to capsaicin, the pungent principle of *Capsicum annuum*, which has been based upon the degradative reactions of this substance,[22] has now received

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[16] S. Smith, *J.*, 1928, 51; W. Nagai and S. Kanao, *J. Pharm. Soc. Japan*, 1928, **48**, 101; *Chem. Zentr.*, 1928, ii, 2553; S. Kanao, *Ber.*, 1930, **63**, [*B*], 95; *A.*, 352.

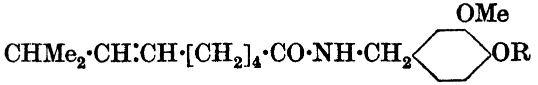
[17] *J.*, 1930, 18, 1232.

[18] P. Rabe, *Ber.*, 1912, **45**, 2166; W. H. Hartung and J. C. Munch, *J. Amer. Chem. Soc.*, 1929, **51**, 2262.

[19] *Annalen*, 1929, **470**, 157; *A.*, 1929, 807.

[20] *J.*, 1929, 2754.

[21] *J.*, 1930, 1390.



(VII.)

confirmation from a synthesis by E. Späth and S. F. Darling.[23] The keto-acid, $CHMe_2{\cdot}CH_2{\cdot}CO{\cdot}[CH_2]_4{\cdot}CO_2H$, from the action of zinc *iso*butyl iodide on the chloride of ethyl hydrogen adipate, was reduced with sodium and alcohol to the corresponding secondary alcohol, from which the bromide, $CHMe_2{\cdot}CH_2{\cdot}CHBr{\cdot}[CH_2]_4{\cdot}CO_2H$, was obtained on heating with fuming hydrobromic acid. The corresponding ester was then distilled with quinoline, and the product was treated successively with sodium hydroxide, thionyl chloride, and veratrylamine to give capsaicin methyl ether (VII; R = Me). Hydrolysis of the latter gave the unsaturated acid,

$$CHMe_2{\cdot}CH{:}CH{\cdot}[CH_2]_4{\cdot}CO_2H,$$

from the chloride of which capsaicin was obtained on interaction with vanillylamine. The position of the double linkage in the aliphatic section of the molecule has been established by oxidation experiments. Spilanthol, the pungent principle of para cress, has hitherto been regarded as the *iso*butylamide of a *n*-nonenecarboxylic acid, yielding *n*-deco*iso*butylamide on the addition of two atoms of hydrogen,[24] but M. Asano and T. Kanematsu [25] have made a further purification of this substance and now believe that it has two atoms of hydrogen less than was originally supposed. Thus it is stated to absorb four atoms of hydrogen when it is converted into *n*-deco*iso*butylamide. Since oxidation with ozone gave succinic acid, *n*-valeric acid, and formic acid, the structure

$$CH_3{\cdot}[CH_2]_3{\cdot}CH{:}C{:}CH{\cdot}[CH_2]_2{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CHMe_2$$

is assigned to it. A product closely related to spilanthol is pellitorine, the pungent principle of *Anacyclus pyrethrum*, which has recently been investigated by J. M. Gulland and G. U. Hopton,[26] who came to the conclusion that it is the *iso*butylamide of a *n*-nonadienecarboxylic acid, $C_9H_{15}{\cdot}CO_2H$, absorbing four atoms of hydrogen on catalytic reduction to give *n*-deco*iso*butylamide. These views are not in entire agreement with those of E. Ott and A. Behr,[27] who have stated that pellitorine is the *iso*butylamide of a *n*-decadienecarboxylic acid, $C_{10}H_{17}{\cdot}CO_2H$.

S. G. P. PLANT.

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[22] See, *e.g.*, E. K. Nelson and L. E. Dawson, *J. Amer. Chem. Soc.*, 1923, **45**, 2179; *A.*, 1923, i, 1108.

[23] *Ber.*, 1930, **63**, [*B*], 737; *A.*, 599.

[24] Y. Asahina and M. Asano, *J. Pharm. Soc. Japan*, 1920, 503; 1922, 85.

[25] *Ibid.*, 1927, No. 544, 521.

[26] *J.*, 1930, 6.

[27] *Ber.*, 1927, **60**, [*B*], 2284; *A.*, 1928, 50.

ANALYTICAL CHEMISTRY.

In addition to the application of chemical reactions to qualitative and quantitative work, the period under review has furnished some definite advances in the utilisation of physical methods for analytical purposes. The magneto-optic method (Faraday effect) has not, so far as we are aware, been applied hitherto to the detection of kations. It has, of course, been utilised for investigations of optical rotation in the magnetic field, but the paper by F. Allison and E. J. Murphy [1] points out a method of test equal to the most delicate of the methods now available. As is well known, the Faraday effect consists in the rotation of the plane of polarisation of light on passing through a liquid, when this is placed in a magnetic field, and it has been supposed that this effect followed immediately on the application of the magnetic field. Allison and his co-workers have produced evidence in favour of a time-lag between the Faraday effect and the magnetic field, the time-lag being utilised for the detection of kations. This is accomplished by using two liquid cells of equal dimensions, so arranged that the alternating electric impulse obtained by means of a high-potential spark between metal electrodes is divided in the electric circuit, so that the optical rotation due to the magnetic field produced in the solenoid wound round the observation cells is in opposite directions. The arrangement of apparatus is such that light, plane polarised through a Nicol prism, passes through the first cell, then traverses the air space to the second cell and passes through this cell, which is followed by another Nicol prism originally crossed so as to extinguish the light from the first prism. Since there is an air gap between the two cells, the light takes a short time (*i.e.*, the distance between the cell centres in cm. divided by 3×10^{10}, the velocity of light) to reach the second cell. The length of the circuit to the winding around the second cell is therefore varied, by means of movable contacts, so that the electric impulse reaches this solenoid in the time equal to that taken for the light to traverse the distance between the centres of the two cells. In the case where the same liquid is used in both cells, no light will pass through the second crossed Nicol with this arrangement of apparatus. Carbon disulphide is chosen as a standard to which other liquids are referred, since it shows the smallest time-lag between the Faraday effect and the magnetic field, and the apparatus is adjusted to zero position with both cells containing this liquid. If now, one cell is filled with another liquid, say carbon tetrachloride, it is found that in order to extinguish the light, or to obtain a sharp minimum of light passing through the second Nicol, it is necessary to move the cell back, or else to alter the length of the electric circuit, which effects the same purpose. The distance through which the cell is moved or the alteration in length of the circuit divided by the velocity of light gives a value for the time-lag of the liquid referred to carbon disulphide as a standard. It was found that each compound, organic or inorganic, has its own time-lag and thus produces a minimum of light at a point characteristic of the compound. Further, in a mixture, each compound retains its own time-lag. Each kation has its own minimum or several minima which appear to depend on the number of isotopes. The chlorides are best adapted for investigation, since the minima are separated farthest in these compounds. An unexpected result of this inquiry was that compounds retained their characteristic minima until the concentration was reduced below 1 in 10^{10}, whereupon the minima faded out. The apparatus has to be calibrated for the kation being sought for, and when this is done it seems to be available for determining solubilities of slightly soluble salts, or for mixtures. Examples of the extent of the time-lags referred to carbon disulphide are the following : zinc chloride (four isotopes) $-6{\cdot}08$, $-6{\cdot}40$, $-6{\cdot}73$, and $-6{\cdot}85 \times 10^{-9}$ sec.; lead chloride (four) $-21{\cdot}90$, $-22{\cdot}07$, $-22{\cdot}30$, and $-22{\cdot}68 \times 10^{-9}$ sec. As the time-lags could be determined within $0{\cdot}2 \times 10^{-9}$ sec. on different occasions, and were much closer for any individual set of experiments, the method appears capable of wide application.

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[1] *J. Amer. Chem. Soc.*, 1930, **52**, 3796; *A.*, 1541.

The use of *X*-rays in quantitative chemical analysis is now taking shape more definitely as a practical means of technical analysis for general laboratory use. Chemical and spectroscopic methods of test depend upon the outer electrons of the atom, while *X*-ray spectra which utilise the *K* and *L* electrons lend themselves especially to "atomic" analysis by reason of the simplicity of the spectra compared with optical spectra. The *X*-ray spectra themselves are unequivocal for the element, since the *K*-line suspected to belong to an element need only be accepted if the whole series of *K*-lines of that element is present. This gives a check on the method at once, and it differs from the optical spectral method which depends in the limit on persistent spectral lines. T. H. Laby [2] has utilised both the *K* and *L* spectra for the detection of impurities in zinc, and is able, in general, to identify metallic elements from chromium (at. no. 24) upwards. He has in this way discovered minute traces of impurities such as gallium, germanium, molybdenum, and tungsten, present in quantities which would escape detection by chemical methods as ordinarily applied to the analysis of spelter. It is pointed out by Laby that the advantages of the method are that one photograph of the *X*-ray spectrum gives all the elements from chromium to uranium, that analysis of chemically similar elements such as the rare earths is more easily carried out, and that the specimen is not consumed in the examination. A communication[3] on the application of *X*-ray spectroscopy to quantitative analysis demonstrates that certain alloys of copper and zinc, tin and cadmium, lead and bismuth, and so on, may be analysed with an accuracy of 0·5% of the constituent, provided the metals are those of close atomic numbers.

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[2] T. H. Laby, *Trans. Faraday Soc.*, 1930, **26**, 497; *A.*, 1141.

Another *X*-ray method for quantitative analysis utilises secondary *X*-rays[4] and a special form of tube so that the substance under investigation is supported on a screen, but is separated from the high vacuum of the tube itself by means of a thin aluminium sheet. An anticathode giving harder radiation than the edges of the absorption band of the element undergoing examination is used to produce the secondary radiation and this is compared with the lines furnished by a standard substance known to be present in definite amount. A table is now available giving the principal comparison lines of the secondary radiation for the elements from sodium to uranium, so that the choice of a suitable standard substance becomes comparatively easy. For this purpose the rare earths offer special advantages, for they are unlikely to occur in any ordinary material which is being examined, thus permitting of their addition in definite amounts without introducing any error due to the sample itself containing the rare earth. This method is claimed to give the proportion of an element which is present to the extent of 1% or so, with an accuracy of 0·01%. A method similar to the foregoing has recently been applied[5] to the determination of potassium in soils with very successful results. In this case a known amount of manganese oxide is incorporated with the soil, and the proportion of potassium found by comparing the intensity photographically of the potassium line $K\alpha_1$ of wave-length 3734 X.U.* with the second-order $K\beta_1$ line of manganese which appears at 3812 X.U.

Of the more recent applications of the optical spectroscopic method, one of the most interesting deals with the determination of cadmium, lead, and iron in zinc.[6] It is shown how quantities of impurities of the order of 0·001 % can be detected and estimated with a fair degree of accuracy in a very short time. The method employs either arc or spark spectra obtained with electrodes of the metal being tested under carefully controlled conditions; the impurity is estimated by comparing visually on the spectrogram, the intensity of a fixed line of the impurity with that of a near-by line due to the zinc itself. Tables are given showing the most suitable lines for examination. Thus, cadmium line λ 2144·4 is compared with zinc line λ 2147·4, and this enables one to estimate the cadmium when present in proportions from 0·1 to 0·001 %. Similarly, lead and iron may be determined within certain limits imposed by considerations of the accuracy of determining intensities of lines on photographic plates. A variation of the method is that employing an " auxiliary " spectrum of some other metal.[7] Thus, in the determination of cadmium in zinc, there is superimposed on the zinc spectrum a spectrum derived from pure tin electrodes, and the slit of the spectrograph is shortened so that short tin lines are readily recognised distributed amongst the longer zinc lines. Pairs of cadmium and tin lines are then chosen of equal intensity and compared with a table showing for different proportions of cadmium in zinc which lines show equal intensity on the photographic plate. The use of a method such as that described enables large numbers of specimens of zinc to be tested rapidly for the impurities mentioned and for any others for which calibration can be effected in a similar manner. It is to be noted that the methods described above give results which are specific for particular elements, and in this respect they possess a definite advantage over most other physical methods applied to the analysis of mixtures, *e.g.*, refractivity or viscosity. There is a further advantage inasmuch as the quantity of material required is small and is not destroyed in the test. In this respect the processes have an advantage over purely chemical methods, but it is not to be inferred, therefore, that the advantage is wholly with the physical methods. These fail to be delicate enough with certain elements such as phosphorus or arsenic, and they are not so good as a chemical method when adequate material for test is available in such cases as the determination of lead, copper, iron, nickel, when these are present in large or in very small proportion of the order of 0·001 %.

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[3] C. E. Eddy and T. H. Laby, *Proc. Roy. Soc.*, 1930, [*A*], **127**, 20; *A.*, 724.

[4] G. von Hevesy, J. Böhm, and A. Faessler, *Z. Physik*, 1930, **63**, 74; *A.*, 1141.

[5] J. T. Calvert, *Trans. Faraday Soc.*, 1930, **26**, 509.

[6] D. M. Smith, *ibid.*, p. 101.

* 1 X.U. = 10^{-11} cm.

An interesting procedure for the identification of volatile organic liquids is furnished by determining the variation of the azeotropism of the binary system consisting of the substance to be identified and some standard pure liquid.[8] The deviation in azeotropism is found from the difference in boiling point of the standard liquid and of the binary azeotrope formed with it. Tables are available showing the limits of azeotropism for hydrocarbons, alcohols, esters, and ketones boiling from 80° to 225°, and for the constants of suitable standard liquids. In some cases two or three binary systems may have to be examined before the unknown liquid can be identified, but the method is fairly rapid and requires little material for examination.

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[7] W. Gerlach, *Z. Metallk.*, 1928, **20**, 248; *Z. anorg. Chem.*, 1924, **142**, 387.

[8] M. Lecat, *Z. physikal. Chem.*, 1930, **146**, 232; *Bull. Acad. roy. Belg.*, 1929, [v], **15**, 1073; *A.*, 724.

When large numbers of determinations of halogens in organic compounds have to be made, the ordinary Carius method, or heating with lime, is slow and rather cumbersome. It was shown some time ago[9] that a modified Kjeldahl method using chromic oxide in addition to sulphuric acid was capable of giving accurate results on the determination of chlorine and bromine. A similar method, but one which is suitable for iodine as well as chlorine and bromine, has now been worked out:[10] it has also been applied successfully to the microchemical determination of halogens and metals[11] in organic compounds. In this process, fuming sulphuric acid, alone or with oxidising reagents, is employed in a special form of apparatus. For chlorine and bromine, the liberation of halogen is complete and it may be trapped in an alkaline arsenite solution for final estimation. With iodine it is necessary to use hydrogen peroxide to obtain free iodine, and some iodic acid may be formed. This is conveniently reduced by means of hydrazine, and the hydriodic acid oxidised to iodine by hydrogen peroxide. The results given for both macro- and micro-determinations are very good. These processes are rapid and capable of being applied readily when numerous determinations have to be made. A further advantage of the second procedure is that the digestion liquid from which the halogen has been expelled is available for determining other elements, particularly metals, present in the compound investigated. This is of special convenience for organic arsenic or antimony compounds. The method is likely to give low results for selenium, for it has been shown[12] that selenium dioxide is appreciably volatile in open vessels. For this reason a modified Carius tube method was devised for organic selenium compounds on the micro-scale and gave very satisfactory results when the precipitated selenium was weighed on a Pregl micro-Gooch crucible. The process was also found suitable for tellurium, but in view of the non-volatility of tellurium dioxide, the decomposition of the telluro-organic compound can be effected in a micro-Kjeldahl flask.

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[9] P. W. Robertson, *J.*, 1916, **109**, 218.

[10] J. J. Thompson and U. O. Oakdale, *J. Amer. Chem. Soc.*, 1930, **52**, 1195; *A.*, 799.

[11] H. H. Willard and J. J. Thompson, *ibid.*, p. 1893; *A.*, 940.

[12] H. D. K. Drew and C. R. Porter, *J.*, 1930, 2091.

Of the numerous applications of the micro-chemical methods of analysis, some of much importance are described in "Mikrochemie, Festschrift, 1930" dedicated to Prof. Friedrich Emich. A preliminary communication [13] deals with the micro-methods for the examination of beryllium silicate rocks working on a few milligrams of sample. No claim for completeness is made, but a definite step forward in micro-mineral analysis is here set out, for it is shown how the following constituents may be separated and determined: phosphoric oxide, aluminium, iron, beryllium, and magnesium. In this analysis the value of 8-hydroxyquinoline as a precipitant for kations is again demonstrated.

An ingenious method of applying the micro-Dumas method for nitrogen determinations, while avoiding the use of a micro-balance, is to weigh out about 0·1 g. of material, and dissolve it in a known amount of some solvent such as carbon tetrachloride. An aliquot portion of the solution is mixed with copper oxide and the solvent is allowed to evaporate away. The impregnated copper oxide is transferred to a micro-Dumas combustion apparatus and the nitrogen determined as usual.[14]

In all precise micro-chemical work, proper facilities, including separate rooms, micro-chemical balances, and the special apparatus necessary for accurate work, are desirable, but it is not so well known that a good ordinary chemical balance can readily be adapted for weighings to less than 0·01 mgm. The balance selected must be of the kind in which the suspension hooks for the pans are supported wholly vertically below the agate planes and knife edges, without bends on the portion of the support rising to the agate planes. A. E. Conrady [15] has shown that by a method of calibration and weighing fully described, which avoids swinging of the pointer, it is possible to obtain weighings with normal loads, capable of being reproduced to less than 0·01 mgm. A simple brake arrestment for the pointer is needed, and this is readily made and attached. The brake is a useful addition to any precision balance since it enables the balance arms and pointer to be released without vibration.

Amongst the papers presented to the symposium on Analytical Chemistry [16] held in Atlanta, Ga., in April 1930, are several important reviews which give succinct accounts of some modern analytical developments. Amongst these are three subjects of increasing interest for analytical chemistry: (1) Applications of photo-electric cells to chemical analysis,[17] which deals briefly with the types of photo-electric cells and their circuits and gives indications of their practical use in chemical investigations involving colorimetry; (2) a review of the progress of potentiometric titrations,[18] which gives an outline of the theory, shows the types of titration apparatus, and displays in an admirable manner the various kinds of titrations for which potentiometric methods have been employed; and (3) conductometric titrations,[19] a short account of some practical methods applied to water analysis, the determination of the acidity of fruit juices, wines, and so on.

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[13] A. Benedetti-Pichler and F. Schreider, Emich Festschrift, 1930, 1.

[14] J. B. Niederl, O. R. Trasitz, and W. J. Saschek, *ibid.*, pp. 219, 232.

[15] *Proc. Roy. Soc.*, 1922, [*A*], **101**, 211.

[16] *Ind. Eng. Chem.* (*Anal.*), 1930, **2**, No. 3.

In this connexion, attention is called to the form of capillary electrode [20] which is suitable for determining the p_H values at a point in plant tissues. The apparatus is a small calomel half-cell fitted to a capillary agar–potassium chloride bridge, capable of use with quinhydrone. Since it is sufficiently compact to be moved about readily, it can be utilised for the exploration of plant tubers.

The employment of ceric sulphate as an oxidising agent in volumetric analysis is extending, for it has the advantage of being more stable than permanganate, is more reactive in the presence of acids, and it can be used in fairly concentrated hydrochloric acid solutions. The only reaction is $Ce^{\cdot\cdot\cdot\cdot}$ to $Ce^{\cdot\cdot\cdot}$, and there are no side reactions. The solution of ceric sulphate in dilute sulphuric acid is readily standardised potentiometrically against ferrous sulphate,[21] or against sodium oxalate.[22] Determinations may be carried out in hot solutions, but in some cases the use of iodine chloride as a catalyst enables the titration to be carried out at lower temperatures. In such cases methylene-blue may be used as an internal indicator for visual titrations. Further applications of ceric sulphate solutions are now available. Thallium can be determined electrometrically in warm hydrochloric acid solutions, the results reported being quite satisfactory.[23] Tellurous acid may also be readily determined provided chromic sulphate is added as a catalyst, a reaction which points to much wider applications.[24] A peculiar selective degree of oxidation of organic acids has also been discovered, for whilst formic, acetic, succinic, fumaric, and maleic acids are not oxidised by ceric sulphate, tartaric, malonic, malic, glycollic, and citric acids are so oxidised, although some peculiarities are to be observed in the proportion of $Ce^{\cdot\cdot\cdot\cdot}$ required per mol. of organic acid.[23] Again, quinol is rapidly and completely oxidised to quinone, with the peculiarity that the electrometric titration proceeds best when the quinol solution is added to the ceric sulphate solution.[25] Useful reversible indicators for the end-point of the titration of ferrous sulphate with ceric sulphate are erio-glaucin A and alkali-fast (erio) green A.[26] These indicators are yellow in ferric solutions and rose-coloured in ceric solutions. A comprehensive bibliography and reference to the use of ceric sulphate up to May 1930 is to be found in Furman's review of potentiometric titrations referred to above.[18]

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[17] H. M. Partridge, *Ind. Eng. Chem.* (*Anal.*), 1930, **2**, 207.

[18] N. H. Furman, *ibid.*, p. 213.

[19] I. M. Kolthoff, *ibid.*, p. 225.

[20] I. M. Robertson and A. M. Smith, *J. Soc. Chem. Ind.*, 1930, **49**, 120T.

[21] N. H. Furman, *J. Amer. Chem. Soc.*, 1928, **50**, 755; *A.*, 1928, 499.

[22] H. H. Willard and (Miss) P. Young, *ibid.*, p. 1322; *A.*, 1928, 725.

[23] *Idem, ibid.*, 1930, **52**, 132; *A.*, 312.

[24] *Idem, ibid.*, p. 555; *A.*, 442.

Inorganic Analysis.

Qualitative.—A mixture of hexamethylenetetramine with potassium iodide forms a more sensitive reagent for the microchemical detection of the heavy metals than "hexamine" alone.[27] Diphenylthiocarbazone forms coloured complex compounds with many heavy metals,[28] whilst lead, bismuth, copper, and cobalt give colorations with viscose solution.[29] Systematic spot-analysis for the commoner metals is further developed,[30] and the effect of the presence of other elements on some microscopical tests for metals has been recorded.[31] A specific reaction for cadmium with nitrophenolarsinic acid is described,[32] and the action of Meurice's bromide–brucine reagent for cadmium on other heavy metals has been investigated.[33]

Variations of a flame test for tin are described,[34] also drop reactions for lead [35] and for the mercurous ion.[36] Colour reactions of somewhat limited value are given by resorcinol with lead,[37] and with zinc.[38] The use of certain phenolic acids has been applied to the detection and separation of the metals of the analytical group

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[25] N. H. Furman and J. H. Wallace, jun., *J. Amer. Chem. Soc.*, 1928, **50**, 1443; *A.*, 727.

[26] *Idem*, *ibid.*, p. 2347; *A.*, 1012.

[27] I. M. Korenman, *Pharm. Zentr.*, 1929, **70**, 709; *A.*, 1929, 1412; compare *idem*, *ibid.*, p. 1; *A.*, 1929, 286.

[28] H. Fischer, *Z. angew. Chem.*, 1929, **42**, 1025; *A.*, 1929, 1412.

[29] J. V. Tamchyna, *Chem. Listy*, 1930, **24**, 31; *A.*, 443.

[30] K. Heller and Z. Fleischhans, *Mikrochem.*, 1930, **8**, 33; *A.*, 443; compare K. Heller and P. Krumholz, *ibid.*, 1929, **7**, 213; *A.*, 1929, 900.

[31] W. F. Whitmore and F. Schneider, *ibid.*, 1930, **8**, 293; *A.*, 1148.

[32] F. Pavelka and E. Kolmer, *ibid.*, p. 277; *A.*, 1147.

[33] I. M. Korenman, *Pharm. Zentr.*, 1929, **70**, 693; *A.*, 1929, 1413.

[34] E. Schröer and A. Balandin, *Z. anorg. Chem.*, 1930, **189**, 258; *A.*, 727; H. Meissner, *Z. anal. Chem.*, 1930, **80**, 247; *A.*, 882; F. L. Hahn, *ibid.*, 1930, **82**, 113.

[35] F. Pavelka, *Mikrochem.*, 1929, **7**, 301; *A.*, 182.

[36] N. A. Tananaev, *Ukrain. Chem. J.*, 1930, **5**, 63; *A.*, 1148.

[37] Ligor Bey and M. Faillebin, *Bull. Soc. chim.*, 1930, [iv], **47**, 225; *A.*, 563.

[38] K. Fabrich, *Verh. Geol. Bundesanst. Wien*, 1929; *A.*, 1147.

IIA.[39] Under suitable conditions, Feigl's rhodanine reagent for silver is very sensitive also for mercury and copper.[40] The compounds of nickel, copper, and cobalt with dithio-oxamide can be utilised in microchemical tests for these metals.[41] Di*iso*nitrosoacetone is a more sensitive reagent for ferrous iron than dimethylglyoxime; [42] reactions of aluminium, iron, chromium, manganese, zinc, nickel, and cobalt with organic reagents are summarised.[43] Bismuth alone interferes with the use of cæsium sulphate as confirmatory reagent in detecting aluminium.[44] A new scheme of separation of the metals of the iron, zinc, barium, and alkali groups in presence of phosphates has been devised.[45] The cobalt–thiocyanate reaction for the detection of these ions has been investigated,[46] and also the composition of the precipitate obtained by the action of ferrocyanide on zinc salts in the presence of cobalt, utilised as a colour test for zinc.[47] The compound $Cs_2[Ni(SeO_3)_2]$, formed by reaction of cæsium chloride and sodium selenite with nickel salts,[48] is distinguished from the similar crystals given with magnesium salts, other than phosphate, by reaction with dimethylglyoxime.[49]

Rapid and trustworthy methods for the detection of the alkaline-earth metals are recommended; [50] with sodium tungstate, barium ions give characteristic octahedra.[51] The bromides of calcium, strontium, and magnesium are soluble in *iso*amyl alcohol, whilst those of barium, sodium, and potassium are almost insoluble.[52] Further details are given of the use of *p*-nitrobenzeneazoresorcinol as a reagent for magnesium,[53] for which thiodiphenylcarbazide has also been used.[54] Magnesium and lithium do not interfere with the detection of potassium as picrate,[55] and further work is recorded on the use of zirconium sulphate as a reagent for potassium [56] and on the triple acetate test for sodium.[57]

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[39] P. N. Das-Gupta, *J. Indian Chem. Soc.*, 1929, **6**, 627; *A.*, 1929, 1412.

[40] I. M. Kolthoff, *J. Amer. Chem. Soc.*, 1930, **52**, 2222; *A.*, 1011; compare *Ann. Reports*, 1929, **26**, 190.

[41] F. Feigl and H. J. Kapulitzas, *Mikrochem.*, 1930, **8**, 239; *A.*, 1147; P. Rây, *Z. anal. Chem.*, 1929, **79**, 94; *A.*, 182.

[42] J. Dubský and M. Kuraš, *Chem. Listy*, 1929, **23**, 496; *A.*, 1929, 1414.

[43] G. Sensi and R. Testori, *Ann. Chim. Appl.*, 1929, **19**, 383; *A.*, 1929, 1413.

[44] H. Yagoda and H. M. Partridge, *J. Amer. Chem. Soc.*, 1930, **52**, 3579; *A.*, 1393.

[45] M. O. Charmandarjan, *Z. anal. Chem.*, 1929, **79**, 90; *A.*, 183.

[46] I. M. Kolthoff, *Mikrochem.*, 1930, **8**, 176; *A.*, 882.

[47] A. Schachkeldian, *J. Russ. Phys. Chem. Soc.*, 1929, **61**, 2217; *A.*, 563.

[48] A. Martini, *Mikrochem.*, 1930, **8**, 41; *A.*, 565.

[49] L. Rosenthaler, *ibid.*, p. 151; *A.*, 881.

[50] P. Agostini and R. Abbiate, *Ann. Chim. Appl.*, 1930, **20**, 229; *A.*, 1147.

[51] G. Denigès, *Bull. Soc. Pharm. Bordeaux*, 1929, **67**, 4; *A.*, 53.

[52] H. Yagoda, *J. Amer. Chem. Soc.*, 1930, **52**, 3068; *A.*, 1264.

[53] E. W. Engel, *ibid.*, p. 1812; *A.*, 881; H. Leitmeier and F. Feigl, *Tsch. Min. Petr. Mitt.*, 1930, **40**, 325; *A.*, 1264.

[54] P. Agostini, *Ann. Chim. Appl.*, 1930, **20**, 235; *A.*, 1147.

[55] E. R. Caley, *J. Amer. Chem. Soc.*, 1930, **52**, 953; *A.*, 562.

Spot-tests for vanadium and tungsten [58] and for the precious metals [59] are described, as also the analytical application of catalytic reactions in the platinum group.[60] Silver azide is dimorphous, crystallising either in needles or in plates.[61] Molybdates give colour reactions with phenylhydrazine [62] and with potassium benzylxanthate.[63] The general analytical behaviour of ekatantalum is described.[64]

Some general schemes for the detection of the principal anions have been devised,[65] including methods for anions containing the cyanogen group.[66] Test-papers for carbonyl chloride are prepared from mixed solutions of dimethyl-*p*-aminobenzaldehyde and diphenylamine.[67] Various methods are proposed for the detection of fluorine in rocks and mineral waters.[68] Reactions for nitrites are given by *apo*morphine, [69] aminosulphonic acid,[70] and aqueous extract of walnut kernels.[71] A silver nitrate–tannin reagent is reduced by even traces of ammonia.[72]

Feigl's azide–iodide reaction is applied as a test for sulphide-sulphur in minerals,[73] and a comparison has been drawn of the sensitivity of various tests for traces of hydrogen sulphide.[74] The formation of methylene iodide from iodoacetic acid and persulphates serves as a delicate test for these salts,[75] whilst hyposulphites give a rose coloration with ammoniacal naphthol-yellow.[76] A colour test for silicate depends upon the formation of a complex silicomolybdate.[77]

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[56] R. D. Reed and J. R. Withrow, *J. Amer. Chem. Soc.*, 1929, **51**, 3238; *A.*, 52; *idem, ibid.*, 1930, **52**, 2666; *A.*, 1150.

[57] V. P. Malitzky and V. A. Tubakaiev, *Mikrochem.*, 1929, **7**, 334; *A.*, 181.

[58] N. A. Tananaev and G. A. Pantchenko, *J. Russ. Phys. Chem. Soc.*, 1929, **61**, 1051; *A.*, 54.

[59] N. A. Tananaev and K. A. Dolgov, *ibid.*, p. 1377; *A.*, 185; H. Holzer, *Mikrochem.*, 1930, **8**, 271; *A.*, 1150.

[60] F. L. Hahn, *ibid.*, p. 77; *A.*, 445; F. Feigl and P. Krumholz, *Ber.*, 1930 **63**, [*B*], 1917; *A.*, 1394.

[61] R. Uzel, *J. Czech. Chem. Comm.*, 1930, **2**, 300; *A.*, 1010.

[62] E. Montignie, *Bull. Soc. chim.*, 1930, [iv], **47**, 128; *A.*, 313.

[63] S. L. Malowan, *Z. anal. Chem.*, 1929, **79**, 201; *A.*, 183.

[64] A. von Grosse, *J. Amer. Chem. Soc.*, 1930, **52**, 1742; *A.*, 883.

[65] P. Agostini, *Ann. Chim. Appl.*, 1929, **19**, 520; *A.*, 311; *idem, ibid.*, 1930, **20**, 112; *A.*, 725; F. E. Raurich, *Anal. Fis. Quim.*, 1930, **28**, 749; *A.*, 1392.

[66] A. Schapovalenko, *Ukrain. Chem. J.*, 1929, **4**, 303; *A.*, 313; *J. Russ. Phys. Chem. Soc.*, 1929, **61**, 2101; *A.*, 562; T. Pavolini, *Ann. Chim. Appl.*, 1929, **19**, 561; *A.*, 444.

[67] A. Suchier, *Z. anal. Chem.*, 1929, **79**, 183; *A.*, 181.

[68] I. P. Alimarin, *ibid.*, 1930, **81**, 8; *A.*, 1143; H. Leitmeier and F. Feigl, *Tsch. Min. Petr. Mitt.*, 1929, **40**, 6; *A.*, 51; J. C. Gil, *Anal. Fis. Quim.* (*Tech.*), 1929, **27**, 141; *A.*, 51.

[69] F. Pavelka, *Mikrochem.*, 1930, **8**, 46; *A.*, 442.

[70] P. Baumgarten and I. Marggraff, *Ber.*, 1930, **63**, [*B*], 1019; *A.*, 880.

[71] P. Zywnev, *Z. anal. Chem.*, 1930, **79**, 389; *A.*, 442.

[72] K. G. Makris, *ibid.*, **81**, 212; *A.*, 1263.

[73] M. Niessner, *Mikrochem.*, 1930, **8**, 121; *A.*, 879; F. Feigl and H. Leitmeier, *Tsch. Min. Petr. Mitt.*, 1929, **40**, 20; *A.*, 51.

Quantitative.—Dichlorofluorescein is a suitable adsorption indicator for the argentometric titration of very dilute chloride solutions; [78] bromophenol-blue and bromocresol-purple may be used in titrating bromides or chlorides with mercurous nitrate.[79] The effect of the presence of various kations in this method has also been investigated.[80] The p_{H} of the colour change of some vegetable indicators is recorded,[81] as also the sensitivity and stability of phthaleins and sulphonephthaleins to alkali,[82] and a stable, sensitive starch indicator.[83] Several other papers deal with indicators.[84] Some aspects of the colorimetric p_{H} determination are discussed.[85]

Borax and mercuric oxide,[86] sodium oxalate,[87] potassium titanium oxalate,[88] and various other compounds [89] have been examined as standards in volumetric analysis, and also the processes occurring in thiosulphate solutions on keeping.[90] The iodine monochloride end-point is used in the titration of iodide[91] and arsenite;[92] bromoiodometric methods are given for urea, ammonium salts, formic acid, and iodides,[92a] and some alkalimetric titrations described.[93] An improved method of determining water in micas has been devised,[94] and also a more general process involving the use of calcium hydride.[95] The sensitivity of various colorimetric reactions of iron, nickel, copper, and silver has been ascertained by an electrochemical method,[96] and the methods of indicating the sensitivity of analytical reactions[97] and methods of indirect analysis are discussed.[98]

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[74] E. C. Truesdale, *Ind. Eng. Chem.* (*Anal.*), 1930, **2**, 299; *A.*, 1144.

[75] G. Panopoulos and A. Petzetakis, *Chem.-Ztg.*, 1930, **54**, 310; *A.*, 735.

[76] E. E. Jelley, *Analyst*, 1930, **55**, 34; *A.*, 181.

[77] F. Feigl and H. Leitmeier, *Tsch. Min. Petr. Mitt.*, 1929, **40**, 1; *A.*, 52.

[78] I. M. Kolthoff, W. M. Lauer, and C. J. Sunde, *J. Amer. Chem. Soc.*, 1929, **51**, 3273; *A.*, 50.

[79] L. von Zombory, *Z. anorg. Chem.*, 1929, **184**, 237; *A.*, 54.

[80] N. P. Rudenko, *J. Russ. Phys. Chem. Soc.*, 1930, **62**, 505; *A.*, 1010.

[81] A. del Campo, A. Rancaño, and G. Subero, *Anal. Fis. Quim.*, 1929, **27**, 587; *A.*, 50; N. P. Sobyanin and S. G. Saakov, *J. Chem. Ind. Russia*, 1929, **6**, 735; *A.*, 1143; O. B. Pratt and H. O. Swartout, *Science*, 1930, **71**, 486; *A.*, 1142.

[82] A. Thiel, *Monatsh.*, 1929, **53** and **54**, 1008; *A.*, 1929, 1410.

[83] M. S. Nichols, *Ind. Eng. Chem.* (*Anal.*), 1929, **1**, 215; *A.*, 1929, 1411.

[84] H. Eichler, *Z. anal. Chem.*, 1929, **79**, 81; *A.*, 181; F. L. Hahn, *ibid.*, 1930, **80**, 321; *A.*, 1009; J. F. Reith, *Pharm. Weekblad*, 1929, **66**, 1097; *A.*, 181; B. Samdahl, *J. Pharm. Chim.*, 1930, [viii], **11**, 8; *A.*, 343; E. E. Harris, H. W. Haugen, and B. E. Fahl, *J. Amer. Chem. Soc.*, 1930, **52**, 2397; *A.*, 1009; A. H. Johnson and J. R. Green, *Ind. Eng. Chem.* (*Anal.*), 1930, **2**, 2; *A.*, 560.

[85] S. F. Acree and E. H. Fawcett, *ibid.*, p. 78; *A.*, 560; L. Wolf, *Z. Elektrochem.*, 1930, **36**, 803; *A.*, 1391.

[86] N. A. Lazarkevitsch, *Ukrain. Chem. J.*, 1929, **4**, 405; *A.*, 309; R. Biazzo and C. Chines, *Ann. Chim. Appl.*, 1930, **20**, 258; *A.*, 1143.

[87] *U.S. Bur. Stand.*, 1930, Circ. 381; *A.*, 726.

[88] W. M. Thornton, jun., and R. Roseman, *Amer. J. Sci.*, 1930, [v], **20**, 14; *A.*, 1009.

[89] Vasterling, *Pharm. Ztg.*, 1930, **75**, 58; *A.*, 182.

Aluminous silicates may be attacked by sintering with small amounts of sodium carbonate,[99] and sulphide minerals by fusion with sodium thiosulphate.[1] Other papers of general interest deal with the segregation of samples for analysis,[2] with the effect of various factors on the separation of metals by fractional precipitation,[3] with modern trends in analytical chemistry,[4] and with analytical separations by ether extraction.[5]

Several volumetric[6] and colorimetric methods of determining copper are described, reagents in the latter class including nitrosochromotropic acid,[7] urolobin,[8] sodium diethyldithiocarbamate,[9] and salicylate-benzidine.[9a] Copper may be weighed in the form of its compound with salicylaldoxime[10] and as the complex $[HgI_4](Cu\ en_2)$;[10a] the precipitation of copper by boiling with thiosulphate has been critically examined,[11] and a rapid method is described for converting cupric into cuprous sulphide.[12]

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[90] F. L. Hahn and H. Clos, *Z. anal. Chem.*, 1929, **79**, 11; *A.*, 51; E. Schulek, *ibid.*, 1930, **80**, 190; *A.*, 725; F. H. Campbell and F. J. Watson, *Chem. Eng. Min. Rev.*, 1930, **22**, 340; *A.*, 1144.

[91] E. H. Swift, *J. Amer. Chem. Soc.*, 1930, **52**, 894; *A.*, 561.

[92] E. H. Swift and C. H. Gregory, *ibid.*, p. 901; *A.*, 561.

[92a] J. H. van der Meulen, *Chem. Weekblad*, 1930, **27**, 550, 558; *A.*, 1392.

[93] C. J. van Nieuwenburg, *ibid.*, pp. 143, 158, 186, 206; *A.*, 879; *idem*, *ibid.*, p. 174; *A.*, 1142; W. Poethke and P. Manicke, *Z. anal. Chem.*, 1929, **79**, 241; *A.*, 311; O. Schewket, *Biochem. Z.*, 1930, **224**, 325; *A.*, 1392.

[94] K. Wiskont and I. Alimarin, *Z. anal. Chem.*, 1929, **79**, 271; *A.*, 310.

[95] O. Notevarp, *ibid.*, 1930, **80**, 21; *A.*, 560.

[96] H. Fritz, *ibid.*, 1929, **78**, 418; *A.*, 1929, 1414.

[97] F. L. Hahn, *Mikrochem.*, 1930, **8**, 75; *A.*, 441; K. Heller, *ibid.*, p. 141; *A.*, 879.

[98] O. Liesche, *Z. angew. Chem.*, 1929, **42**, 1109; *A.*, 310; P. Fuchs, *Z. anal. Chem.*, 1930, **79**, 417; *A.*, 441; O. Liesche, *ibid.*, **81**, 273.

[99] A. N. Finn and J. F. Klekotka, *Bur. Stand. J. Res.*, 1930, **4**, 809; *A.*, 1010.

[1] E. Donath, *Chem.-Ztg.*, 1930, **54**, 78; *A.*, 311.

[2] G. F. Smith, L. V. Hardy, and E. L. Gard, *Ind. Eng. Chem.* (*Anal.*), 1929, **1**, 228; *A.*, 1929, 1409.

[3] O. Ruff, *Oesterr. Chem.-Ztg.*, 1929, **32**, 199; *A.*, 180.

[4] H. H. Willard, *Ind. Eng. Chem.* (*Anal.*), 1930, **2**, 201; *A.*, 1142; L. Moser, *Monatsh.*, 1929, **53** and **54**, 39; *A.*, 1929, 1410.

[5] O. von Grossmann, *Chem.-Ztg.*, 1930, **54**, 402; *A.*, 879.

[6] A. T. Küchlin, *Rec. trav. chim.*, 1930, **49**, 151; *A.*, 313; W. Orlik and W. Tietze, *Chem.-Ztg.*, 1930, **54**, 174; *A.*, 444; M. Lora y Tomayo, *Anal. Fis. Quim.*, 1930, **28**, 63; *A.*, 444; J. Golse, *Bull. Soc. chim.*, 1930, [iv], **47**, 655; *A.*, 1148.

Precipitation of lead as sulphate yields accurate results only when the solution is free from ferric and potassium salts, chlorides, and bromides;[13] the chromate method has also been investigated.[14]

Sodium bismuthate may be evaluated by a gasometric method;[15] bismuth can be quantitatively precipitated as the complex $[BiI_4](Co\ en_3)I$[16] or by means of selenious acid, which also precipitates titanium.[17]

Cadmium may be weighed as the hydrated oxalate[18] or as the compound $CdI_2,2[(CH_2)_6N_4,C_3H_5]I$.[19]

Cupferron precipitates mercurous ions quantitatively from nitric acid solutions;[20] mercuric salts are reduced to mercurous chloride by hypophosphorous acid in presence of hydrochloric acid and hydrogen peroxide[21] or to metal by hydrazine or stannous chloride.[22]

Studies of the Gutzeit method for arsenic have been made.[23] An iodometric determination of quinquevalent antimony is described,[24] and a colorimetric method for tin, utilising stannic sulphide.[25] Arsenic, antimony, and tin may be separated by successive distillations under appropriate conditions; [26] in the separation of lead and antimony sulphides by digestion with sodium sulphides, sufficient polysulphide must be present to convert the antimony into thioantimonate.[27]

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[7] E. Cherbuliez and S. Ansbacher, *Helv. Chim. Acta*, 1930, **13**, 187; *A.*, 564.

[8] A. Emmerie, *Chem. Weekblad*, 1930, **27**, 552; *A.*, 1393.

[9] T. Callan and J. A. R. Henderson, *Analyst*, 1929, **54**, 650; *A.*, 53.

[9a] A. B. Schachkeldian, *J. Appl. Chem. Russia*, 1929, **2**, 475; *A.*, 444.

[10] F. Ephraim, *Ber.*, 1930, **63**, [*B*], 1928; *A.*, 1393.

[10a] G. Spacu and G. Suciu, *Z. anal. Chem.*, 1929, **79**, 329; *A.*, 1929, 1413.

[11] J. Majdel, *ibid.*, p. 38; *A.*, 53.

[12] F. L. Hahn, *Ber.*, 1930, **63**, [*B*], 1616; *A.*, 1011.

[13] Z. Karaoglanov and B. Sagortschev, *Z. anal. Chem.*, 1930, **81**, 275; *A.*, 1393; Z. Karaoglanov, *Ber.*, 1930, **63**, [*B*], 597; *A.*, 563.

[14] Z. Karaoglanov and B. Sagortschev, *loc. cit.*; B. Jones, *Analyst*, 1930, **55**, 318; *A.*, 881.

[15] T. Somiya and K. Kawai, *J. Soc. Chem. Ind. Japan*, 1929, **32**, 249B; *A.*, 184.

[16] G. Spacu and G. Suciu, *Z. anal. Chem.*, 1929, **79**, 196; *A.*, 184.

[17] R. Berg and M. Teitelbaum, *Z. anorg. Chem.*, 1930, **189**, 101; *A.*, 566.

[18] J. Dick, *Z. anal. Chem.*, 1929, **78**, 414; *A.*, 1929, 1412.

[19] V. Evrard, *Natuurwetensch. Tijds.*, 1929, **11**, 191; *A.*, 182.

[20] A. Pinkus and (Mlle.) M. Katzenstein, *Bull. Soc. chim. Belg.*, 1930, **39**, 179; *A.*, 1011.

[21] E. Cattelain, *J. Pharm. Chim.*, 1930, [viii], **11**, 580; *A.*, 1148.

[22] H. H. Willard and A. W. Boldyreff, *J. Amer. Chem. Soc.*, 1930, **52**, 569; *A.*, 444; Jean, *Bull. Soc. Pharm. Bordeaux*, 1929, **67**, 239; *A.*, 1148.

[23] A. J. Lindsey, *Analyst*, 1930, **55**, 503; *A.*, 1263; J. W. Barnes and C. W. Murray, *Ind. Eng. Chem.* (*Anal.*), 1930, **2**, 29; *A.*, 562; F. Martin and J. Pien, *Bull. Soc. chim.*, 1930, [iv], **47**, 646; *A.*, 1144.

[24] L. Szebellédy, *Z. anal. Chem.*, 1930, **81**, 36; *A.*, 1150.

It has been found that aluminium hydroxide, precipitated from alkaline solutions by carbon dioxide, is easily washed and filtered; [28] the hydroxide should be ignited at about 1300° to yield a non-hygroscopic oxide.[29] Blum's method can be applied to aluminoborosilicates without the necessity of previous removal of boron.[30] Aluminium is quantitatively precipitated by hydrazine carbonate,[31] whereby separation from iron [32] and manganese [32a] may be effected; this precipitant has also been used for beryllium.[33] Precipitation by means of " fusible white precipitate " has been extended to a number of separations.[34] In the determination of aluminium by means of aurintricarboxylic acid, maximum colour intensity is attained at p_H 4.[35] Some volumetric methods for iron are given; [36] iron and manganese may be separated from aluminium and phosphate by means of sodium hydroxide and hydrogen peroxide.[37] Orthophosphates do not interfere with the colour formation of ferric thiocyanate as much as pyrophosphates.[38] A rapid iodometric determination of chromium in the presence of organic substances has been devised.[39] Titanium is quantitatively precipitated from feebly acid or ammoniacal tartrate solutions by 8-hydroxyquinoline; [40] details

[25] R. Hanssen, *Chem.-Ztg.*, 1930, **54,** 143; *A.*, 445.

[26] H. Biltz, *Z. anal. Chem.*, 1930, **81,** 82; *A.*, 1144.

[27] *Idem, ibid.*, p. 81; *A.*, 1147.

[28] R. Fricke and K. Meyring, *Z. anorg. Chem.*, 1930, **188,** 127; *A.*, 727.

[29] W. Miehr, P. Koch, and J. Kratzert, *Z. angew. Chem.*, 1930, **43,** 250; *A.*, 564; W. Biltz, *ibid.*, p. 370; *A.*, 1148.

[30] O. V. Krasnovski, *Z. anal. Chem.*, 1929, **79,** 175; *A.*, 183.

[31] A. Jílek and J. Lukas, *J. Czech. Chem. Comm.*, 1930, **2,** 63; *A.*, 444.

[32] *Idem, ibid.*, p. 161; *A.*, 727.

[32a] *Idem, ibid.*, p. 113; *A.*, 564.

[33] A. Jílek and J. Koťa, *ibid.*, p. 571; *A.*, 1393.

[34] B. Šolaja, *Z. anal. Chem.*, 1930, **80,** 334; *A.*, 1012; B. Šolaja, M. Kranjčević, and M. Kockar, *Arhiv Hemiju*, 1930, **4,** 136; *A.*, 1149.

[35] O. B. Winter, W. E. Thurn, and O. D. Bird, *J. Amer. Chem. Soc.*, 1929, **51,** 2721; *A.*, 1929, 1413.

[36] F. L. Hahn and H. Clos, *Z. anal. Chem.*, 1929, **79,** 26; *A.*, 54; L. Szebellédy, *ibid.*, 1930, **81,** 26; *A.*, 1149; *idem, ibid.*, p. 97; *A.*, 1149.

[37] I. S. Teletov and N. N. Andronikova, *Ukrain. Chem. J.*, 1929, **4,** 341; *A.*, 313; *Z. anal. Chem.*, 1930, **80,** 351; *A.*, 1012.

[38] G. W. Leeper, *Analyst*, 1930, **55,** 370; *A.*, 1012.

[39] F. Feigl, K. Klanfer, and L. Weidenfeld, *Z. anal. Chem.*, 1930, **80,** 5; *A.*, 565.

[40] R. Berg and M. Teitelbaum, *ibid.*, **81,** 1; *A.*, 1150.

are given for the separation of titanium from other metals [41] and for a colorimetric method of determining this element with gallic acid.[42]

The precipitation of manganese by von Knorre's persulphate method has been examined from the gravimetric [43] and volumetric [44] standpoint, as also the influence of cobalt on the bismuthate method for manganese.[45] Two iodometric methods for zinc are described.[46]

Colorimetric methods of determining cobalt are given; [47] the insoluble hydrazine–thiocyanate compounds may be employed for the determination of cobalt, nickel, and cadmium.[48] Phenylthiohydantoic acid has been further investigated as a precipitant for cobalt,[49] and two volumetric methods for cobalt are described.[50]

Small amounts of calcium may be determined after separation as triple nitrite with potassium nickelonitrite [51] or as tungstate.[52] Various aspects of the oxalate method for calcium have been considered and it is shown that the oxalate may be converted quantitatively into the carbonate at 450° to 500°. This observation provides a great simplification in the determination of calcium.[53] Barium chloride can be titrated in neutral or acid solution with alkali sulphate with sodium rhodizonate as indicator.[54]

The conversion of magnesium ammonium phosphate into pyrophosphate is stated to occur below 480°, thus allowing the use of sintered-glass crucibles.[55] On the other hand, the results of a comprehensive inquiry into the methods of obtaining $Mg_2P_2O_7$ demonstrate that a certain concentration of ammonium salts must be observed. It is further shown that for accurate work ignition to constant weight at 1100° is desirable. Even at 1000° constant weight results slowly, especially with large precipitates, while at 1200° there is a definite loss of weight and low results are obtained. The observation is made that it is more difficult to obtain constant weight in determinations of magnesium than in determinations of phosphorus.[56] The alkali precipitation method for determining magnesium has been investigated.[57]

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[41] L. Moser, K. Neumayer, and K. Winter, *Monatsh.*, 1930, **55**, 85; *A.*, 727.

[42] P. N. Das-Gupta, *J. Indian Chem. Soc.*, 1929, **6**, 855; *A.*, 566.

[43] J. Majdel, *Z. anal. Chem.*, 1930, **81**, 14; *A.*, 1149.

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[48] P. B. Sarkar and B. K. Datta-Ray, *J. Indian Chem. Soc.*, 1930, **7**, 251; *A.*, 882.

[49] V. Cuvelier, *Natuurwetensch. Tijds.*, 1929, **11**, 131; *A.*, 1929, 1414.

[50] S. Glasstone and J. C. Speakman, *Analyst*, 1930, **55**, 93; *A.*, 445; A. A. Vassiliev, *Z. anal. Chem.*, 1929, **78**, 439; *A.*, 1929, 1414.

[51] A. Astruc and M. Mousseron, *Compt. rend.*, 1930, **190**, 1558; *A.*, 1011.

[52] A. Astruc, M. Mousseron, and (Mlle.) N. Bouissou, *ibid.*, p. 376; *A.*, 443; M. Mousseron and (Mlle.) N. Bouissou, *Bull. Soc. Chim. biol.*, 1930, **12**, 482; *A.*, 1011.

[53] H. H. Willard and A. W. Boldyreff, *J. Amer. Chem. Soc.*, 1930, **52**, 1888; *A.*, 881; J. T. Dobbins and W. M. Mebane, *ibid.*, p. 1469; *A.*, 726; M. Stiller, *Chem.-Ztg.*, 1930, **54**, 422; *A.*, 1147; Z. Herrmann, *Z. anorg. Chem.*, 1929, **184**, 289; *A.*, 52.

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The triple acetate method for sodium [58] and the cobaltinitrite method for potassium [59] continue to attract attention. Other methods for the latter metal utilise the per-rhenate,[60] and triple lead cobaltinitrites.[61]

The precipitation of indium and its separation from various other metals are described.[62] Precipitation with camphoric acid affords a separation of gallium from numerous other metals ; [63] three methods are given for the separation of gallium and aluminium.[64] Uranium may be determined colorimetrically with gallic acid,[65] or gravimetrically following treatment with tannic acid [66] or with 8-hydroxyquinoline ; [67] the latter reagent also precipitates thorium from acetic acid solution. Ignition of lanthanum oxalate at 450° results in the formation of a basic carbonate.[68] Further studies are recorded of the determination of zirconium and beryllium as phosphates,[69] and of the analytical chemistry of tantalum, niobium, and their mineral associates.[70] Precipitation with tannin and antipyrine permits the separation of tungsten from various metals,[71] with arsenic acid from vanadium,[72] and with benzidine from arsenates.[73] A rapid reaction, catalysed by phosphates, occurs between vanadyl sulphate and potassium iodate in hot alkaline solution.[74]

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[56] J. J. Hoffman and G. E. F. Lundell, *U.S. Bur. Stand. J. Res.*, 1930, **5**, 279.

[57] T. Maeda and R. Syôzi, *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1930, **13**, 185; *A.*, 881.

[58] H. H. Barber and I. M. Kolthoff, *J. Amer. Chem. Soc.*, 1929, **51**, 3233; *A.*, 52; E. R. Caley, *Ind. Eng. Chem.* (*Anal.*), 1929, **1**, 191; *A.*, 1929, 1412; *idem*, *J. Amer. Chem. Soc.*, 1930, **52**, 1349; *A.*, 726; E. Kahane, *J. Pharm. Chim.*, 1930, [viii], **11**, 425; *A.*, 880; *idem*, *Bull. Soc. chim.*, 1930, [iv], **47**, 382; *A.*, 726.

[59] L. Bonneau, *ibid.*, 1929, [iv], **45**, 798; *A.*, 49; A. Vassiliev and N. Matveev, *Z. anal. Chem.*, 1930, **81**, 106; *A.*, 1146.

[60] H. Tollert, *Naturwiss.*, 1930, **18**, 849; *A.*, 1392.

[61] P. S. Sergeenko, *Ukrain. Chem. J.*, 1930, **5**(Sci.), 113; *A.*, 1146; V. I. Tovarnitzki and P. S. Sergeenko, *Zhur. Sakharnoi Prom.*, 1928, **2**, 228; *A.*, 52.

[62] L. Moser and F. Siegmann, *Monatsh.*, 1930, **55**, 14; *A.*, 564.

[63] S. Ato, *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1930, **12**, 225; *A.*, 564.

[64] *Idem*, *ibid.*, **14**, 35; *A.*, 1264.

[65] R. N. Das-Gupta, *J. Indian Chem. Soc.*, 1929, **6**, 763; *A.*, 183.

[66] *Idem*, *ibid.*, p. 777; *A.*, 183.

[67] F. Hecht and W. Reich-Rohrwig, *Monatsh.*, 1929, **53** and **54**, 596; *A.*, 1929, 1415.

Osmium and ruthenium may be separated through the differing solubility in aqueous alcohol of their complexes with strychnine.[75] Ruthenium may be quantitatively precipitated by sodium bicarbonate.[76] Minute quantities of gold may be separated from much iron, lead, and copper by deposition on silk; [77] volumetric methods are given for small amounts of silver.[78]

Polonium may be separated from radium-*E* and -*D*, and radium-*E* from radium-*D*, by deposition on silver and nickel respectively, even when present in unweighable amounts.[79]

Further work has been carried out on rubidium chlorostannate; [80] anhydrous dioxan [81] or acetone [82] serves to extract lithium chloride from certain other chlorides. Small quantities of lithium may be determined nephelometrically as stearate [83] or centrifugally as phosphate.[84]

A study has been made of the separation of thallium from ter- and quadri-valent metals.[85]

Volumetric methods for determining thiocyanate by means of permanganate,[86] hypobromite,[87] and iodine or iodate [88] have been investigated, whilst oxidation for gravimetric purposes may be effected by hydrogen peroxide in hot alkaline solution.[89] Neutral 5% potassium chlorate solution, whilst hardly affecting hydrogen sulphide, oxidises sulphur dioxide quantitatively when air containing these gases is passed through it.[90] Conditions for the reduction of sulphate to sulphide by means of calcium hydride are prescribed,[91] and a similar reduction by hydriodic acid is followed by colorimetric comparison by Caro's reaction for small quantities; [92] reduction by zinc dust is applied to the determination of sulphate in the presence of aluminium fluoride.[93] The precipitation of barium sulphate under varying conditions has been studied, and the resulting precipitates have been examined microscopically.[94] Persulphate is recommended as a standard oxidising agent in iodometric determinations.[95]

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[68] H. J. Backer and K. H. Klaassens, *Z. anal. Chem.*, 1930, **81**, 104; *A.*, 1148.

[69] O. Ruff and E. Stephan, *Z. anorg. Chem.*, 1929, **185**, 217; *A.*, 184.

[70] W. R. Schoeller and H. W. Webb, *Analyst*, 1929, **54**, 704; *A.*, 184.

[71] L. Moser and W. Blaustein, *Monatsh.*, 1929, **52**, 351; *A.*, 312.

[72] A. Jílek and J. Lukas, *Chem. Listy*, 1930, **24**, 73; *A.*, 565.

[73] *Idem, ibid.*, p. 320; *A.*, 1265.

[74] J. B. Ramsey and A. Robinson, *J. Amer. Chem. Soc.*, 1930, **52**, 480; *A.*, 445.

[75] S. C. Ogburn, jun., and L. F. Miller, *ibid.*, p. 42; *A.*, 313.

[76] R. Gilchrist, *Bur. Stand. J. Res.*, 1929, **3**, 993; *A.*, 446.

[77] J. Donau, *Mikrochem.*, 1930, **8**, 257; *A.*, 1150.

[78] J. Golse, *Bull. Soc. chim.*, 1930, [iv], **47**, 760; *A.*, 1264; W. Holwech, *Tidsskr. Kjemi Berg.*, 1930, **10**, 78; *A.*, 1392.

[79] O. Erbacher and K. Philipp, *Z. physikal. Chem.*, 1930, **150**, 214; *A.*, 1394.

[80] E. Burkser, W. L. Milgevskaja, and R. W. Feldmann, *Z. anal. Chem.*, 1930, **80**, 264; *A.*, 881.

[81] A. Sinka, *ibid.*, p. 430; *A.*, 1146.

[82] M. H. Brown and J. H. Reedy, *Ind. Eng. Chem.* (*Anal.*), 1930, **2**, 304; *A.*, 1146.

[83] E. R. Caley, *J. Amer. Chem. Soc.*, 1930, **52**, 2754; *A.*, 1146.

[84] B. Brauner, *J. Czech. Chem. Comm.*, 1930, **2**, 442; *A.*, 1146.

[85] L. Moser and W. Reif, *Monatsh.*, 1929, **52**, 343; *A.*, 312.

The influence of phosphates and of iron on the determination of silica by Diénert and Wandenbulcke's colorimetric method has been studied,[96] as also the alkalimetric titration of fluosilicic and fluoboric acids.[97]

A number of volumetric methods for determining cyanides are discussed; [98] ferric chloride is applied as external indicator in the titration of ferrocyanide with zinc.[99] Perchloric acid is recommended for liberating carbon dioxide from carbonates, a special apparatus being described.[1]

Several papers have appeared dealing with the determination of fluoride,[2] of perchlorate,[3] the halogenides,[4] and the phosphorus acids generally.[5]

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[86] J. Golse, *Bull. Soc. Pharm. Bordeaux*, 1929, **67**, 226; *A.*, 1144; B. Reinitzer and H. Pollet, *Z. anal. Chem.*, 1930, **81**, 286; *A.*, 1391; K. Schröder, *ibid.*, p. 308; *A.*, 1392.

[87] J. Golse, *Bull. Soc. Pharm. Bordeaux*, 1929, **67**, 221; *A.*, 1144.

[88] H. A. Pagel and O. C. Ames, *J. Amer. Chem. Soc.*, 1930, **52**, 2698; *A.*, 1144.

[89] F. Schuster, *Z. anorg. Chem.*, 1930, **186**, 253; *A.*, 442.

[90] V. G. Gurevitsch, *J. Russ. Phys. Chem. Soc.*, 1930, **62**, 111; *A.*, 879.

[91] W. F. Caldwell with F. C. Krauskopf, *J. Amer. Chem. Soc.*, 1929, **51**, 2936; *A.*, 1929, 1411.

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[93] H. Ginsberg, *Z. angew. Chem.*, 1930, **43**, 21; *A.*, 441.

[94] S. Popov and E. W. Neuman, *Ind. Eng. Chem. (Anal.)*, 1930, **2**, 45; *A.*, 561.

[95] C. V. King and E. Jette, *J. Amer. Chem. Soc.*, 1930, **52**, 608; *A.*, 441.

[96] L. A. Thayer, *Ind. Eng. Chem. (Anal.)*, 1930, **2**, 276; *A.*, 1145.

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[99] P. F. Felkers, *Chem. Weekblad*, 1930, **27**, 209; *A.*, 882.

[1] C. A. Jacobson and J. W. Haught, *Ind. Eng. Chem. (Anal.)*, 1930, **2**, 334; *A.*, 1145.

Reduction to ammonia is applied to the determination of nitrates and nitrites,[6] and of nitrogen itself in gaseous mixtures.[7] Ferric chloride may be used as indicator in the titration of soluble azides with sodium nitrite.[8]

Organic Analysis.

Qualitative.—M. Wagenaar [9] describes microchemical reactions of (*a*) strychnine, (*b*) brucine, (*c*) hydrastine, (*d*) berberine, (*e*) aconitine, (*f*) cytisine, (*g*) cocaine, and (*h*) veratrine; similar tests are described for codeine and dionine,[10] antifebrin and phenacetin,[11] antipyrine,[12] homatropine and novatropine,[13] thiophen,[14] strychnine,[15] ephedrine,[16] barbituric acid derivatives,[17] glycine,[18] cysteine,[19] pyridine,[20] *iso*propyl alcohol,[21] acetone and formaldehyde,[22] α-naphthol,[23] Michler's ketone,[24] mono-alkyl- and -aryl-arsinic acids,[25] adrenaline,[26] and various compounds of pharmaceutical interest.[27] Rufianic acid precipitates many organic bases,[28] but the compounds with the alkaloids are all very similar in appearance; [29] other precipitants for alkaloids are described.[30]

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[2] E. Carrière and Janssens, *Compt. rend.*, 1930, **190**, 1127; *A.*, 879; E. Carrière and Rouanet, *ibid.*, 1929, **189**, 1281; *A.*, 180; J. Casares, *Anal. Fis. Quim.* (*tech.*), 1929, **27**, 290; *A.*, 180; J. G. Fairchild, *J. Washington Acad. Sci.*, 1930, **20**, 141; *A.*, 725.

[3] K. Heller, K. Willingshofer, and B. Sadrawetz, *Z. anal. Chem.*, 1929, **79**, 256; *A.*, 310; H. H. Willard and J. J. Thompson, *Ind. Eng. Chem.* (*Anal.*), 1930, **2**, 272; *A.*, 1143.

[4] R. Lang and J. Messinger, *Ber.*, 1930, **63**, [*B*], 1429; *A.*, 1010; R. G. Turner, *J. Amer. Chem. Soc.*, 1930, **52**, 2768; *A.*, 1143; S. V. Gorbatschev and I. A. Kasatkina, *Z. anorg. Chem.*, 1930, **191**, 104; *A.*, 1143; K. Kuchler, *Chem.-Ztg.*, 1930, **54**, 582; *A.*, 1143; H. Szancer, *Arch. Pharm.*, 1930, **268**, 263; *A.*, 725; G. G. Longinescu and T. I. Pirtea, *Bull. Acad. Sci. Roumaine*, 1929, **12**, No. 7—10, 57; *A.*, 561; R. H. Klein, *Analyst*, 1930, **55**, 192; *A.*, 561; R. Hofmann, *Pharm. Zentr.*, 1930, **71**, 18; *A.*, 310; H. Ditz and R. May, *Z. anal. Chem.*, 1930, **79**, 333; *A.*, 310; *idem, ibid.*, p. 371; *B.*, 417.

[5] H. Egnér, *Svensk Kem. Tidskr.*, 1929, **41**, 240; *A.*, 1929, 1412; T. Kuttner and L. Lichtenstein, *J. Biol. Chem.*, 1930, **86**, 671; *A.*, 725; K. Hinsberg and D. Laszlo, *Biochem. Z.*, 1930, **217**, 346; *A.*, 562; L. Brestak and O. A. Dafert, *Z. angew. Chem.*, 1930, **43**, 216; *A.*, 562; A. Dunaiev, *Z. anal. Chem.*, 1930, **80**, 252; *A.*, 880; R. Zinzadze, *Z. Pflanz. Düng.*, 1930, **16**, [*A*], 129; *A.*, 725; A. P. Dunaev, *Min. Suir. Tzvet. Met.*, 1929, 424; *A.*, 1010.

[6] K. Woidich, *Oesterr. Chem.-Ztg.*, 1929, **32**, 183; *A.*, 1929, 1411.

[7] S. N. Blumstein, *Z. anal. Chem.*, 1930, **79**, 324; *A.*, 311.

[8] J. F. Reith and J. H. A. Bouwman, *Pharm. Weekblad*, 1930, **67**, 475; *A.*, 880.

[9] *Pharm. Weekblad*, 1929, **66**, (*a*) p. 1073; (*b*) p. 1170; 1930, **67**, (*c*) p. 57, (*d*) p. 77, (*e*) p. 165, (*f*) p. 205, (*g*) p. 229, (*h*) p. 393; *A.*, 98, 229, 353, 353, 486, 629, 623, 796, respectively.

[10] G. de Haas, *ibid.*, p. 508; *A.*, 937.

[11] L. Ekkert, *Pharm. Zentr.*, 1930, **71**, 179; *A.*, 629.

[12] *Idem, ibid.*, p. 180; *A.*, 617.

[13] *Idem, ibid.*, p. 641; *A.*, 1461.

[14] *Idem, ibid.*, p. 625; *A.*, 1460.

[15] J. C. Ward and J. C. Munch, *J. Amer. Pharm. Assoc.*, 1930, **19**, 954; *A.*, 1456.

For purposes of identification, derivatives are described of various alcohols with 4′-iododiphenyl-4-carbimide [31] and with 3 : 5-dinitrobenzoyl chloride,[32] of organic acids with *p*-phenylphenacyl bromide,[33] of aldehydes and ketones with 2 : 4-dinitrophenylhydrazine,[34] of aldehydes with hippuric acid,[35] of aryl aldehydes with indandione,[36] of nitriles with magnesium phenyl bromide,[37] of mercaptans with mercuric bromide, with 3 : 5-dinitrobenzoyl chloride, and with 3-nitrophthalic anhydride,[38] and of tertiary amines with benzyl chloride and with methyl *p*-toluene sulphonate.[39]

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[16] J. Sivadjian, *J. Pharm. Chim.*, 1930, [viii], **12**, 266; *A.*, 1460.

[17] L. van Itallie and A. J. Steenhauer, *Pharm. Weekblad*, 1930, **67**, 977; *A.*, 1460; G. Denigès, *Bull. Soc. Pharm. Bordeaux*, 1929, **67**, 165; *A.*, 788.

[18] W. Zimmermann, *Z. physiol. Chem.*, 1930, **189**, 4; *A.*, 897.

[19] R. Fleming, *Biochem. J.*, 1930, **27**, 965; *A.*, 1420.

[20] J. V. Kulikov and T. N. Krestovosdvigenskaja, *Z. anal. Chem.*, 1930, **79**, 452; *A.*, 489.

[21] H. Leffmann and C. C. Pines, *Bull. Wagner Inst. Sci.*, 1929, **4**, 47; *A.*, 318.

[22] *Idem, ibid.*, p. 39; *A.*, 1929, 1425; L. Kofler and H. Hilbck, *Mikrochem.*, 1930, **8**, 117; *A.*, 940.

[23] O. Carletti, *Giorn. Chim. Ind. Appl.*, 1930, **12**, 178; *A.*, 908.

[24] H. Gilman, O. R. Sweeney, and L. L. Heck, *J. Amer. Chem. Soc.*, 1930, **52**, 1064; *A.*, 778.

[25] J. Golse, *Bull. Soc. Pharm. Bordeaux*, 1929, **67**, 84; *A.*, 442.

[26] H. Bierry and B. Gouzon, *Compt. rend.*, 1930, **190**, 1239; *A.*, 941.

[27] L. Rosenthaler, *Pharm.-Ztg.*, 1930, **75**, 650; *A.*, 941; C. van Zijp, *Pharm. Weekblad*, 1930, **67**, 189; *A.*, 629.

[28] W. Zimmermann, *Z. physiol. Chem.*, 1930, **188**, 180; **189**, 155; *A.*, 941, 1170.

[29] L. Rosenthaler, *Pharm. Zentr.*, 1930, **71**, 561; *B.*, 1090.

[30] *Idem, Amer. J. Pharm.*, 1929, **101**, 724; *A.*, 98; G. D. Lander, *Analyst*, 1930, **55**, 474; *A.*, 1304.

[31] S. Kawai and K. Tamura, *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1930, **13**, 260, 270; *A.*, 1159.

[32] G. B. Malone and E. E. Reid, *J. Amer. Chem. Soc.*, 1929, **51**, 3424; *A.*, 58.

[33] N. L. Drake and J. Bronitsky, *ibid.*, 1930, **52**, 3715; *A.*, 1436.

[34] C. F. H. Allen, *ibid.*, p. 2955; *A.*, 1175.

[35] W. M. Rodionov and A. J. Korolev, *Z. angew. Chem.*, 1929, **42**, 1091; *A.*, 194.

[36] M. V. Ionescu, *Bull. Soc. chim.*, 1930, [iv], **47**, 210; *A.*, 606.

[37] R. L. Shriner and T. A. Turner, *J. Amer. Chem. Soc.*, 1930, **52**, 1267; *A.*, 777.

[38] E. Wertheim, *ibid.*, 1929, **51**, 3661; *A.*, 192.

[39] C. S. Marvel, E. W. Scott, and K. L. Amstutz, *ibid.*, p. 3638; *A.*, 199.

The formation of aniline formate serves to identify formic acid,[40] whilst several tests for acetic acid are given.[41] Acids, including lactones and anhydrides, may be distinguished from phenols by distillation with zinc dust in a current of hydrogen,[42] and neutral tartrates and citrates from the acid salts by means of ammonium metavanadate.[43]

Colour reactions of the sugars have been investigated,[44] as have also derivatives suitable for identification of δ-ketorhamnonic acid.[45]

Nascent iodine gives colorations with certain aromatic amines.[46]

Quantitative.—Further examination has been made of possible sources of error in organic elementary analysis.[47] Investigations on the elementary analysis of organic compounds may be reviewed under the following heads: carbon and hydrogen,[48] nitrogen,[49] halogens generally,[50] and iodine in particular, especially when present in small amount,[51] sulphur,[52] arsenic,[53] and mercury.[54] Improvements and modifications have been made in the hydrogenation process of determining nitrogen,[55] sulphur,[56] and oxygen.[57]

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[40] M. Masriera, *Anal. Fís. Quím.*, 1930, **28**, 916; *A.*, 1405.

[41] D. Krüger and E. Tschirch, *Chem.-Ztg.*, 1930, **54**, 42; *A.*, 357; *Mikrochem.*, 1929, **7**, 318; *A.*, 192; *Ber.*, 1929, **62**, [*B*], 2776; *A.*, 62; K. Serke, *Apoth.-Ztg.*, 1929, **44**, 1018; *A.*, 489.

[42] A. W. van der Haar, *Rec. trav. chim.*, 1929, **48**, 1170; *A.*, 62.

[43] L. Rossi, *Quim. e Ind.*, 1929, **6**, 113; *A.*, 357.

[44] H. Szancer, *Pharm. Zentr.*, 1929, **70**, 645, 663, 665; *A.*, 1929, 1426; S. Tashiro and E. B. Tietz, *J. Biol. Chem.*, 1930, **87**, 307; *A.*, 1198.

[45] E. Votoček and S. Malachta, *Anal. Fís. Quím.*, 1929, **27**, 494; *A.*, 66.

[46] W. Ruziczka, *Z. anal. Chem.*, 1930, **80**, 185; *A.*, 903.

[47] J. Lindner and F. Hernler, *Ber.*, 1930, **63**, [*B*], 949, 1123, 1396, 1672; *A.*, 726, 940, 1031, 1198.

[48] A. Boivin, *Bull. Soc. Chim. biol.*, 1929, **11**, 1269; *A.*, 442; K. Lindenfeld, *Rocz. Chem.*, 1930, **10**, 84; *A.*, 489; E. V. Zappi and A. Manini, *Anal. Asoc. Quím. Argentina*, 1929, **17**, 234; *A.*, 940; M. Nicloux, *Compt. rend. Soc. Biol.*, 1929, **102**, 693; *A.*, 1392; S. Avery and D. Hayman, *Ind. Eng. Chem.* (*Anal.*), 1930, **2**, 336; *A.*, 1198; J. Meyer and Tischbierek, *Z. anal. Chem.*, 1930, **80**, 241; *A.*, 940.

[49] G. Dorfmüller, *Z. Ver. deut. Zucker-Ind.*, 1930, **80**, 407; *A.*, 1166; F. C. Koch, *J. Biol. Chem.*, 1929, **84**, 601; *A.*, 101; B. Flaschenträger, *Mikrochem.*, 1930, **8**, 1; *A.*, 489; E. Zunz, *Ann. Soc. Zymol.*, 1929, **1**, 236; *A.*, 489.

[50] J. J. Thompson, *J. Amer. Chem. Soc.*, 1930, **52**, 3466; *A.*, 1303; P. W. Robertson, *ibid.*, p. 3023; *A.*, 1303; G. Illari, *Ann. Chim. Appl.*, 1929, **19**, 443; *A.*, 101; L. Palfray and (Mlle.) D. Sontag, *Bull. Soc. chim.*, 1930, [iv], **47**, 118; *A.*, 357; S. Sabetay and J. Bléger, *ibid.*, p. 114; *A.*, 318; K. V. Alekseevski and Y. S. Pikazin, *J. Appl. Chem. Russia*, 1930, **3**, 273; *A.*, 1460. See also p. 207.

[51] K. Wülfert, *Mikrochem.*, 1930, **8**, 100; *A.*, 441; J. F. Reith, *Pharm. Weekblad*, 1929, **66**, 829; *A.*, 1929, 1410.

[52] H. Zahnd and H. T. Clarke, *J. Amer. Chem. Soc.*, 1930, **52**, 3275; *A.*, 1303; E. Wertheim, *ibid.*, pp. 1075, 1086; *A.*, 799; H. Emerson, *ibid.*, p. 1291; *A.*, 799.

[53] T. von Fellenberg, *Mitt. Lebensm. Hyg.*, 1929, **20**, 321; *A.*, 1198; *Biochem. Z.*, 1930, **218**, 283; *A.*, 799.

[54] J. J. Rutgers, *Compt. rend.*, 1930, **190**, 746; *A.*, 629.

A critical account and bibliography of methods for the identification and determination of methyl alcohol in presence of ethyl alcohol are given,[58] as also are methods for the determination of small quantities of saturated alcohols.[59]

Some iodometric methods have been examined [60] and also some analytical reactions of lead tetraethyl.[61] Quantitative methods for the following acids are described : tartaric,[62] citric in the presence of some other organic acids,[63] oxalic in stomach contents,[64] and aliphatic mercapto-acids.[65]

Nicotine may be precipitated and weighed in the form of its tetrachloroiodide ; [66] antipyrine and pyramidone, but not the products of boiling the latter with hydrogen peroxide, give sparingly soluble picrates.[67] Quantitative methods, mostly colorimetric, are described for chlorophyll,[68] cholesterol,[69] carotinoids,[70] cerebrosides,[71] choline,[72] arginine,[73] cystine,[74] proteins,[75] trypaflavin and rivanol,[76] rhamnose,[77] and starch.[78] A method for the determination of monosaccharrides in presence of lactose involves the use of buffered Barfoed solution; [79] under specified conditions, aldose sugars use or remove two equivalents of iodine and three of alkali.[80] The effect of dextrose and sucrose on the determination of lævulose by Nijn's method is recorded.[81] The process of Baudouin and Lewin for the micro-determination of dextrose has been improved by the addition of barium sulphate, which greatly facilitates dissolution of the mercury.[82] The micro-determination of various xanthyl derivatives by complete oxidation with sulphuric and iodic acids has been worked out.[83] Primary arsinic acids may be determined volumetrically with thymolphthalein as indicator in the presence of sodium chloride; [84] volumetric processes are described for diphenylchloroarsine and diphenylarsine oxide, alone or in admixture.[85]

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[55] H. ter Meulen, *Rec. trav. chim.*, 1930, **49**, 396; *A.*, 629.

[56] H. ter Meulen, H. F. Opwyrda, and H. J. Ravenswaay, *Chem. Weekblad*, 1930, **27**, 19; *A.*, 357.

[57] H. ter Meulen, H. J. Ravenswaay, and J. R. G. de Veer, *ibid.*, p. 18; *A.*, 357.

[58] A. Ionesco-Matiu and C. Popesco, *J. Pharm. Chim.*, 1930, [viii], **12**, 63; *A.*, 1303.

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[60] W. H. Hatcher and W. H. Mueller, *Trans. Roy. Soc. Canada*, 1929, [iii], **23**, III, 35; *A.*, 324; R. Signer, *Helv. Chim. Acta*, 1930, **13**, 43; *A.*, 323.

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[63] A. I. Kogan, *ibid.*, p. 112; *A.*, 743.

[64] G. D. Elsdon and J. R. Stubbs, *Analyst*, 1930, **55**, 321; *A.*, 941.

[65] E. Larsson, *Z. anal. Chem.*, 1929, **79**, 170; *A.*, 234.

[66] F. D. Chattaway and G. D. Parkes, *J.*, 1929, 2817; *A.*, 227.

[67] S. Erikson, *Svensk Farm. Tidskr.*, 1930, **34**, 1; *A.*, 1199.

[68] H. B. Sprague and L. B. Troxler, *Science*, 1930, **71**, 666; *A.*, 1199.

[69] R. Okey, *J. Biol. Chem.*, 1930, **88**, 367; *A.*, 1303.

[70] H. von Euler, H. Hellström, and M. Rydbom, *Mikrochem.*, 1929, Pregl Fest., 69; *A.*, 1929, 1474.

[71] P. Kimmelstiel, *ibid.*, p. 165; *A.*, 1929, 1474.

[72] W. Roman, *Biochem. Z.*, 1930, **219**, 218; *A.*, 752.

[73] C. J. Weber, *J. Biol. Chem.*, 1930, **86**, 217; *A.*, 755.

[74] C. Rimington, *Biochem. J.*, 1930, **24**, 1114; *A.*, 1420.

[75] R. Winternitz and Z. Stary, *Mikrochem.*, 1930, **8**, 252; *A.*, 1199.

[76] M. J. Schulte, *Pharm. Weekblad*, 1930, **67**, 809; *A.*, 1304.

Guaiacol carbonate is quantitatively brominated in methyl-alcoholic solution; [86] quinol and pyrocatechol are quantitatively oxidised by ferric chloride to quinones, which may be determined iodometrically, the method being applicable in the presence of phenol, resorcinol, and certain other phenols.[87]

Physical Methods.

Slight turbidity in the solution affects the measurements of optical activity; [88] a special polarimeter is described whereby minute concentrations of lævulose and of dextrose can be accurately determined.[89] An optical method for measuring the mercury content of air has been devised, based on the extent of absorption of the mercury line 2537 Å.[90] Sublimation points of numerous substances are recorded at atmospheric pressure and in a vacuum, together with typical photomicrographs.[91] Immersion of transparent solids in liquids of approximately the same refractive index causes them to appear various shades of blue when observed through the microscope.[92] The technique and application of rotation dispersion to the solution of chemical problems are reviewed.[93] The magnitude of the photo-electric current generated in the filament of a neon lamp can be used to indicate the end-point of titrations involving colour changes or precipitations.[94]

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[77] R. A. McCance, *Biochem. J.*, 1929, **23**, 1172; *A.*, 325.

[78] L. Paloheimo, *Biochem. Z.*, 1930, **222**, 150; *A.*, 1167.

[79] O. Svanberg, *Z. physiol. Chem.*, 1930, **189**, 219; *A.*, 894.

[80] C. S. Slater and S. F. Acree, *Ind. Eng. Chem.* (*Anal.*), 1930, **2**, 274; *A.*, 1165.

[81] F. W. Zerban and L. Sattler, *ibid.*, p. 307; *A.*, 1165.

[82] P. Fleury and J. Marque, *J. Pharm. Chim.*, 1929, [viii], **10**, 292; *A.*, 1929, 1426.

[83] L. Cuny and J. Robert, *ibid.*, 1930, [viii], **11**, 241; *A.*, 629.

[84] H. King and G. V. Rutterford, *J.*, 1930, 2138; *A.*, 1461.

[85] E. D. G. Frahm and H. L. Boogaert, *Rec. trav. chim.*, 1930, **49**, 623; *A.*, 941.

[86] L. H. Chernoff, *J. Amer. Chem. Soc.*, 1929, **51**, 3072; *A.*, 1929, 1441.

[87] F. Böck and G. Lock, *Monatsh.*, 1929, **53** and **54**, 888; *A.*, 1929, 1474.

[88] H. K. Miller and J. C. Andrews, *Ind. Eng. Chem.* (*Anal.*), 1930, **2**, 283; *A.*, 1142.

[89] J. W. Meijer, *Rev. Sci. Instr.*, 1930, **2**, 69; *A.*, 581.

[90] K. Müller and P. Pringsheim, *Naturwiss.*, 1930, **18**, 364; *A.*, 727.

Colorimetric methods of analysis are discussed under the headings of true colorimetry, nephelometry, and titrimetric methods; [95] some other papers dealing with nephelometry are recorded.[96]

Much work has been carried out on spectrographic methods of analysis; [97] Löwe's interferometer is applied to the determination of alkalis in minerals.[98]

Electrolytic.—Thallium is deposited on the anode from a solution containing hydrofluoric acid as an adherent film approximating to Tl_2O_3,HF.[99] The use of Wood's metal as cathode has been extended to include the determination of tin, silver, iron, nickel, cobalt, and thallium.[1] Two schemes are recorded to avoid the use of platinum electrodes in the electro-analysis of copper.[2] Other work in this section deals with nickel, cobalt and zinc,[3] sodium, potassium, and calcium,[4] lead and bismuth,[5] and various metals by "internal electrolysis." [6]

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[91] H. Hoffmann, jun., and W. C. Johnson, *J. Assoc. Off. Agric. Chem.*, 1930, **13**, 367; *A.*, 1263.

[92] H. Wagner, *Z. angew. Chem.*, 1930, **43**, 686; *A.*, 1263.

[93] G. Kortüm, *ibid.*, p. 341; *A.*, 728.

[94] T. Somiya and S. Shiraishi, *J. Soc. Chem. Ind. Japan*, 1930, **33**, 300B; *A.*, 1263.

[95] N. Schoorl, *Chem. Weekblad*, 1930, **27**, 52; *A.*, 309.

[96] J. Erdös, *Z. anal. Chem.*, 1930, **80**, 122; *A.*, 724; L. T. Fairhall and J. R. Richardson, *J. Amer. Chem. Soc.*, 1930, **52**, 938; *A.*, 563; J. A. de Loureiro, *Biochem. Z.*, 1930, **224**, 337; *A.*, 1391; F. Rimattei, *J. Pharm. Chim.*, 1929, [viii], **10**, 349; *A.*, 1929, 1410.

[97] H. Lundegårdh, *Arkiv Kemi, Min., Geol.*, 1929, **10**, [*A*], No. 1; *A.*, 311; *Svensk Kem. Tidskr.*, 1930, **42**, 51; *A.*, 560; B. A. Lomakin, *Z. anorg. Chem.*, 1930, **187**, 75; *A.*, 445; B. de la Roche, *Bull. Soc. chim.*, 1930, [iv], **47**, 660; *A.*, 1145; P. Urbain, *Compt. rend.*, 1930, **190**, 940; *A.*, 728; J. Papish, L. E. Hoag, and W. E. Snee, *Ind. Eng. Chem. (Anal.)*, 1930, **2**, 263; *A.*, 1143; J. Papish and D. A. Holt, *Z. anorg. Chem.*, 1930, **192**, 90; *A.*, 1393; H. Lucas, *Physikal. Z.*, 1930, **31**, 803; *A.*, 1264; S. Piña de Rubies and J. Dorronsoro, *Anal. Fis. Quim.*, 1929, **27**, 778; *A.*, 183; G. Piccardi, *Atti R. Accad. Lincei*, 1929, [vi], **10**, 258; *A.*, 313; A. Corsi, *Nuovo Cim.*, 1929, **6**, 275; *A.*, 441.

[98] G. Burger, *Monatsh.*, 1929, **53** and **54**, 985; *A.*, 1929, 1411.

[99] A. Jílek and J. Lukas, *Chem. Listy*, 1930, **24**, 223, 245; *A.*, 1147.

[1] H. Paweck and W. Stricks, *Z. anal. Chem.*, 1929, **79**, 115; *A.*, 184.

[2] P. S. Tutundžić, *Z. anorg. Chem.*, 1930, **190**, 59; *A.*, 882; J. Guzmán and A. Rancaño, *Anal. Fis. Quim. (tech.)*, 1929, **27**, 269; *A.*, 183.

[3] B. Tougarinov, *Bull. Soc. chim. Belg.*, 1930, **39**, 331; *A.*, 1394.

Potentiometric.—Attention is drawn to some important points in the determination of hydrogen-ion concentration.[7] The reactions have been followed between sodium hydroxide and copper sulphate,[8] ferrous or ferric chloride,[9] and aluminium and magnesium chlorides, present together; [10] and in the last instance also that with sodium fluoride. Some applications of the titration of mercurous nitrate with alkali oxalates are described; [11] several papers deal with acid–alkali titrations.[12] Methods have been described for the potentiometric determination of selenium, tellurium, and gold,[13] of gold and platinum,[14] nickel,[15] zinc,[16] arsenic, antimony, tin, and thallium,[17] and copper.[18]

In a series of argentometric studies, the determination of iodides and bromides in chlorides,[19] and of halides in presence of sulphites,[20] has been described. Conditions are prescribed for the titration of phosphates, arsenates, and arsenites with silver nitrate,[21] and of alkali sulphides with sodium nitroprusside.[22]

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[4] A. Belák and Z. von Alföldy, *Biochem. Z.*, 1929, **214**, 110; *A.*, 52.

[5] E. M. Collin, *Analyst*, 1929, **54**, 654; *A.*, 53.

[6] H. J. S. Sand, *ibid.*, 1930, **55**, 309; *A.*, 880.

[7] I. M. Kolthoff and T. Kameda, *J. Amer. Chem. Soc.*, 1929, **51**, 2888; *A.*, 1929, 1410; L. Fletcher and J. B. Westwood, *J. Soc. Chem. Ind.*, 1930, **49**, 201T; *A.*, 1009.

[8] R. Tomii, E. Okabe, and S. Takeda, *Bull. Dept. Appl. Chem. Waseda Univ. Japan*, 1929, **9**, 6; *A.*, 564.

[9] L. W. Elder, jun., *Amer. Electrochem. Soc.*, 1930, May; *A.*, 565.

[10] W. D. Treadwell with E. Bernasconi, *Helv. Chim. Acta*, 1930, **13**, 500; *A.*, 1149.

[11] C. Mayr and G. Burger, *Monatsh.*, 1929, **53** and **54**, 493; *A.*, 1929, 1413; *ibid.*, 1930, **56**, 113; *A.*, 1264.

[12] A. Ríus y Miró, *Anal. Fís. Quím.*, 1929, **27**, 605; *A.*, 50; I. I. Shukov and V. M. Gortikov, *Z. Elektrochem.*, 1929, **35**, 853; *J. Russ. Phys. Chem. Soc.*, 1929, **61**, 2055; *A.*, 50; M. L. Holt and L. Kahlenberg, *Amer. Electrochem. Soc.*, 1930, May; *A.*, 724; F. L. Hahn and R. Klockmann, *Z. physikal. Chem.*, 1930, **146**, 373; *A.*, 560; B. L. Clarke and L. A. Wooten, *J. Physical Chem.*, 1929, **33**, 1468; *A.*, 1929, 1410; F. L. Hahn, *Z. angew. Chem.*, 1930, **43**, 712; *A.*, 1263; S. Linda and J. Ettinger, *Rocz. Chem.*, 1929, **9**, 504; *A.*, 1929, 1411.

[13] K. Someya, *Sci. Rep. Tôhoku Imp. Univ.*, 1930, **19**, 123; *A.*, 725; *Z. anorg. Chem.*, 1930, **187**, 337.

[14] E. Müller and W. Stein, *Z. Elektrochem.*, 1930, **36**, 220, 376; *A.*, 728, 1013; E. Zintl, *ibid.*, p. 551; *A.*, 1265.

[15] T. Heczko, *Z. anal. Chem.*, 1929, **78**, 325; *A.*, 1929, 1415.

[16] S. Saitō, *Bull. Inst. Phys. Chem. Res. Tokyo*, 1929, **8**, 921; *A.*, 53; N. Joassart and E. Leclerc, *Bull. Soc. chim. Belg.*, 1930, **39**, 231; *A.*, 1011.

[17] C. del Fresno and L. Valdés, *Anal. Fís. Quím.*, 1929, **27**, 595; *A.*, 51.

[18] (Miss) M. E. Pring and J. F. Spencer, *Analyst*, 1930, **55**, 375; *A.*, 1011.

[19] O. Tomíček and A. Jánský, *Coll. Czech. Chem. Comm.*, 1929, **1**, 585; *A.*, 51; *ibid.*, 1930, **2**, 1, *A.*, 310.

[20] *Idem*, *ibid.*, 582; *A.*, 50.

Conductometric.—The titration between sulphate and barium acetate and between ferrocyanide and zinc chloride may be followed in boiling, neutral solution by replacing the usual telephone by a system whereby the current is measured by a galvanometer.[23] The most important applications of conductometric titrations have been summarised.[24]

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[21] M. H. Bedford, (Miss) F. R. Lamb, and W. E. Spicer, *J. Amer. Chem. Soc.*, 1930, **52**, 583; *A.*, 442.

[22] G. Scagliarini and P. Pratesi, *Atti R. Accad. Lincei*, 1930, [vi], **11**, 193; *A.*, 726.

[23] G. Jander, *Z. angew. Chem.*, 1929, **42**, 1037; *A.*, 51; G. Jander, A. Pfundt, and H. Schorstein, *ibid.*, 1930, **43**, 507; *A.*, 1142.

[24] I. M. Kolthoff, *Ind. Eng. Chem.* (*Anal.*), 1930, **2**, 225; *A.*, 1142.

BIOCHEMISTRY.

Metabolism of Moulds.

THE marked increase in the amount of research devoted to a study of the metabolic product of moulds since the war can be traced to the curious fact that in the case of nearly all the chemical compounds produced by fermentation methods, there is no alternative, satisfactory, purely chemical method of preparation. The industrial importance of such processes, therefore, cannot be over-emphasised, and it is noteworthy that the researches of Raistrick and his co-workers on the biochemistry of micro-organisms which are mentioned later in this Report were carried out between the years 1922 and 1929 in the laboratories of Nobel's Explosives Company at Ardeer, and are now published as 18 consecutive papers in a special number of the *Philosophical Transactions.*[1]

Carbon Balance Sheets.—Of the two classes of micro-organisms (bacteria and true fungi) which can be readily cultivated in artificial media, much attention has been paid in the past to the chemical activities of the bacteria,[1a] and of the family of true fungi known as the yeasts, but very little to the other classes of true fungi known as the " moulds." In recent years an increasing amount of work on the metabolism of the moulds, especially the production of acids, has been published,[2] but in 1922 it seemed to Raistrick and his co-workers, who wished to make a general survey of the metabolic products of moulds, that it would be impossible to investigate in detail, in any reasonable period of time, the chemical compounds formed by even a small proportion of the different known species of fungi. For this reason, then, instead of attempting the isolation and identification of the compounds formed by any mould taken at random, it was decided to investigate quantitatively the *types* of compounds formed by each of a large number of fungi, so as to obtain a logical basis for the choice of any particular fungus for later investigation. To this end a so-called " carbon balance sheet " was prepared for every species that it was proposed to study : this was found to be of great utility, for it gave a clean-cut classification of the various types of product formed and of their quantitative relationships. In order to reduce the scope of the work, and to ensure the possibility of repetition, all experiments were carried out with glucose as the sole source of carbon in a Czapek–Dox synthetic medium. In this respect the work differs somewhat from that of other investigators.

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[1] *Phil. Trans.*, 1930, **220**, 1.

[1a] Compare Marjory Stephenson, " Bacterial Metabolism," London, 1930.

[2] Compare *Ann. Reports*, 1927, **24**, 222.

The balance sheets show the location, after the metabolism, of all the carbon originally present as glucose in the culture solution. For the practical details of the method the reader must refer to the original paper :[3] it is possible here to mention but briefly the ten *types* of compound in which the carbon is estimated. These are (1) evolved carbon dioxide, (2) gases other than carbon dioxide, (3) volatile products such as ethyl alcohol, etc., (4) the mycelium, (5) total carbon in the metabolism solution, which was further subdivided into (*a*) residual glucose, (*b*) dissolved carbon dioxide, (*c*) volatile acids, (*d*) non-volatile acids, (*e*) carbon compounds precipitable by iron, *e.g.*, proteins, (*f*) carbon unaccounted for.

By means of the carbon balance sheets it has been possible to eliminate from further investigation all those fungi—constituting by far the greater number—which, under the conditions of the experiment, produce practically nothing but carbon dioxide from glucose. In all, some 96 species of *Aspergillus*,[4] 75 species of *Penicillium*, 8 species of *Citromyces*,[5] 23 species of *Fusarium*,[6] and 36 miscellaneous species of fungi[7] have been examined, and from them a choice of species suitable for further intensive investigation has been made. The general results obtained can be summarised as follows.[8]

1. The carbon balance sheets may be used as a biochemical method for the classification of different species in certain families of fungi. This is particularly so in the case of the *Aspergilli*, in which a classification based on biochemical characteristics follows closely that founded on morphological observation. With species of *Fusarium*, however, there is little hope of a biochemical classification, for each of the species tried gave rise principally to ethyl alcohol and showed close alliance with the yeasts.

2. Some light is thrown on the biochemistry of the initial stages of the breakdown of the glucose molecule by fungi. It appears that

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[3] J. H. Birkinshaw and H. Raistrick, *Phil. Trans.*, 1930, **220**, Pt. 2.

[4] J. H. Birkinshaw, J. H. V. Charles, H. Raistrick, and J. A. R. Stoyle, *ibid.*, Pt. 3.

[5] J. H. Birkinshaw, J. H. V. Charles, A. C. Hetherington, H. Raistrick, and C. Thom, *ibid.*, Pt. 4.

[6] J. H. Birkinshaw, J. H. V. Charles, H. Raistrick, and J. A. R. Stoyle, *ibid.*, Pt. 5.

[7] J. H. Birkinshaw, J. H. V. Charles, A. C. Hetherington, and H. Raistrick, *ibid.*, Pt. 6.

[8] H. Raistrick and W. Rintoul, *ibid.*, Pt. 1.

the first step is a Cannizzaro reaction involving the formation from two molecules of glucose of one molecule of mannitol and one molecule of gluconic acid. Depending then on whether the mould in question prefers for growth an acid or a neutral medium, either mannitol or gluconic acid (of course, in some cases both) is destroyed. Thus a certain species of white *Aspergillus* which gives rise to yields of mannitol approximating to, but never exceeding, 50% of the glucose metabolised produces very little if any gluconic acid, refuses to grow in an acid medium, and even when cultivated on a medium with an initial p_H of 4·6 changes this during the course of its growth to 6·5—7. On the other hand, species such as *Aspergillus Wentii* and *Penicillium chrysogenum*, which produce large quantities of gluconic acid, give little or no mannitol, on which material they grow quite well, but in all cases bring the p_H of the medium down to about 1—2. Other species again produce moderate amounts of both these substances.

The production of these two materials from glucose raises an interesting stereochemical point. Glucose on reduction should give sorbitol, and on oxidation, gluconic acid; mannose on similar treatment, mannitol and mannonic acid. Yet in spite of frequent search for sorbitol and mannonic acid as metabolic products of fungi no trace of them has been found.

3. Perhaps the most striking fact is the extraordinary specificity of some of the mould products. It would appear that certain general biochemical reactions such as the production from glucose of mannitol or gluconic acid, of ethyl alcohol, of citric and oxalic acids may be regarded as common to many species belonging to many different families of fungi, but at the same time there are certain highly specific substances which are produced, in some cases by a single species, and in others by a very small sub-group containing a very few species. Citrinin, for instance, is specific for *Penicillium citrinum* Thom, and may be used as a test for this species by the purely chemical test of adding ferric chloride to the metabolism solution, whereupon a characteristic iodine brown colour is produced. All these specific products, some of which are referred to briefly later, are more complex than glucose and are good illustrations of the amazing synthetic powers of these organisms.

Metabolic Products of Moulds.

Oxalic, Citric, and Gluconic Acids.—It is now generally recognised that these three acids are produced by most moulds, and that the second two are not as specific as was at first suspected.

Succinic Acid.—Raistrick and his co-workers [9] have found that this acid is formed in small amounts from sugar by several species of *Aspergillus* and *Fumago vagans*. It was isolated as the ester, and identified as the free acid and anhydride. Its production by *Rhizopus* species growing on a medium containing acetates has been shown by T. Takahashi and K. Asai [10] and W. S. Butkevitsch and M. W. Federov.[11] Using the calcium salt of *n*-butyric acid as a source of carbon for the growth of *A. niger*, H. B. Stent, V. Subramaniam, and T. K. Walker [12] have isolated, with other products, succinic acid, which was identified by its m. p. and conversion into di-*p*-nitrobenzyl succinate. They consider that the butyric acid first undergoes β-oxidation with the production of acetone. Further oxidation yields acetic acid, which then undergoes dehydrogenation according to the Thunberg–Wieland hypothesis :

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[9] J. H. Birkinshaw and H. Raistrick, *Phil. Trans.*, 1930, **220**, Pt. 17.

$$3CH_3{\cdot}CO{\cdot}CH_3 \longrightarrow CH_3{\cdot}CO{\cdot}CO_2H + 2CH_3{\cdot}CO_2H \longrightarrow$$
$$CH_3{\cdot}CH(OH){\cdot}CO_2H + CO_2H{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$$

Fumaric Acid.—This was first observed by F. Ehrlich [13] in 1911 to be a product of *Mucor stolonifer*. Recently W. S. Butkevitsch and M. W. Federov [14] claim to have obtained good yields of this acid when the organism is grown on solutions of glycerol, acetic acid and sugar. C. Wehmer [15] in 1918 obtained good yields from sugar by a species of *Aspergillus* which he named *A. fumaricus*. In a culture reported to be this species Raistrick and his co-workers failed to obtain fumaric acid, and it is worthy of note that in a recent paper Wehmer [16] states that his culture, which originally gave large amounts of this acid, now produces only traces of this substance, and that gluconic acid is now formed instead. A similar experience is related by R. Schreyer.[17] His culture of *A. fumaricus* has in the course of time lost its power of producing fumaric acid, and now gives rise to citric and gluconic acids. It would appear that we have in this an interesting case of evolutionary change of metabolism.

The claim of A. Gottschalk [18] that *Rhizopus nigricans* when grown on a solution of pyruvic acid gave rise to fumaric acid was disputed by F. Ehrlich and I. Bender,[19] who state that no growth takes place on such a medium. This has now been admitted by

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[10] *Bull. Agric. Chem. Soc. Japan*, 1928, 113.

[11] *Biochem. Z.*, 1930, **219**, 87; *A.*, 643.

[12] *J.*, 1929, 1987, 2485; *A.*, 1929, 1271; 1930, 66.

[13] *Ber.*, 1911, **44**, 3737.

[14] *Biochem. Z.*, 1929, **207**, 302; 1930, **219**, 87; *A.*, 1929, 724; 1930, 643.

[15] *Ber.*, 1918, **51**, 1663.

[16] *Biochem. Z.*, 1928, **197**, 418; *A.*, 1928, 1164.

[17] *Ibid.*, 1928, **202**, 131; *A.*, 1929, 217.

[18] *Z. physiol. Chem.*, 1926, **152**, 136; *A.*, 1926, 545.

[19] *Ibid.*, 1927, **170**, 118; **172**, 314; *A.*, 1928, 95; 1928, 804.

Gottschalk and confirmed by W. S. Butkevitsch and M. W. Federov,[20] who state that in the presence of calcium carbonate, which was a constituent of the nutrient solution, pyruvic acid undergoes a change to a monobasic acid of empirical formula $C_7H_6O_4$, which bears no relationship to the activity of the mould.

Malic Acid.—Casual references to the production of this acid by moulds occur in the earlier literarure. C. Wehmer [16] has now shown definitely that it is produced in small amounts from sugar by *Aspergillus fumaricus.* Raistrick and his co-workers [21] also have isolated the acid as its ester from the products of a white species of *Aspergillus*, and also from *A. Wentii* growing on glucose.

The biochemical inter-relationship between succinic, fumaric and malic acids was referred to in a previous Report.[21a] It would appear that similar inter-conversion can be brought about mycologically. T. Takahashi and K. Sakaguchi [22] have shown that a *Rhizopus* species can convert fumaric into *l*-malic acid, and can also bring about the reverse change. F. Challenger and L. Klein [23] have shown that a strain of *A. niger* affords excellent yields exclusively of *l*-malic acid when grown upon a fumarate medium. They therefore conclude that the enzyme fumarase is secreted by the organism. Using the same strain of *A. niger* and a succinate medium, H. B. Stent, V. Subramaniam, and T. K. Walker [24] obtained a mixture of *dl*-malic and *l*-malic acids. As oxidation of succinic acid by hydrogen peroxide in the presence of ferrous sulphate yields as a first stage malic acid, they consider that this *dl*-malic acid [25] owes its formation to the direct hydroxylation of the succinic acid, a process which they think could be effected by an aerobic oxydase system. The *l*-malic acid, however, they consider has arisen through a preliminary dehydrogenation of the succinic acid to fumaric acid, which is then acted on by the fumarase, and not to any preferential utilisation of the *d*-isomeride by the mould growing on the *dl*-malic acid. It is interesting to note that Ruhland and Wetzel (p. 246) find an accumulation of both *dl*-malic and *l*-malic acid in developing rhubarb stalks.

Mannitol.—Although the presence of mannitol in the mycelium of fungi has long been recognised, it appears to have been considered simply as a reserve food comparable with the glycogen of yeast and not as a definite fermentation product. Raistrick and his co-workers [26] have now shown that it is produced by many moulds, and by certain species of white *Aspergillus* in particular, in yields as high as 50% of the sugar metabolised. The alcohol [27] was estimated in presence of glucose by a method depending on the increased rotation observed when borax was added to the solution, allowance being made for the fact, hitherto unrecorded, that glucose in 0·9% concentration in 6% borax solution is optically inactive and at concentrations up to 0·9% is lævorotatory. It was found that culture solutions in which the amount of aeration was unrestricted gave only small yields, and the high values quoted above were only obtained when the amount of aeration was strictly limited.

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[20] *Biochem. Z.*, 1929, **206**, 440; *A.*, 1929, 607.

[21] J. H. Birkinshaw and H. Raistrick, *Phil. Trans.*, 1930, **220**, Pt. 17.

[21a] *Ann. Reports*, 1928, **25**, 226.

[22] *Bull. Agric. Chem. Soc. Japan*, 1927, **3**, 59.

[23] *J.*, 1929, 1644; *A.*, 1929, 1165.

[24] *Ibid.*, p. 1987; *A.*, 1929, 1271.

[25] *Ibid.*, p. 2485; *A.*, 1930, 66.

Polysaccharides.—A few polysaccharides from the lower fungi have been previously recorded, and given appropriate names, but attempts to find out their constitution have been limited to showing the reaction, if any, to iodine and the sugar given on hydrolysis. Raistrick and his co-workers [28] have encountered several such substances in the course of their work. From a species of *Aspergillus* they have isolated what appears to be glycogen.[27]

From *Fumago vagans* [21] they have isolated a new substance, which separates from water as a white amorphous precipitate, and from the mycelium of *Penicillium digitatum*, Saccardo,[29] a similar substance which is insoluble in cold, but moderately soluble in hot water. These two substances give no colour with iodine, have an empirical formula $C_6H_{10}O_5$, and in aqueous solution are neutral and strongly dextrorotatory. They give rise quantitatively to glucose on hydrolysis with dilute acids, and are unaffected by invertase or diastase.

The most interesting product, however, is that formed from *Penicillium luteum*, Zukal, a mucilage which the authors have named " luteic " acid.[30] The crude product as first isolated is the magnesium salt of a complex organic acid, and from this the pure acid, a white amorphous mass resembling starch, was eventually prepared. It gives a gelatinous solution in water and does not react with alkaline iodine, reduce Benedict's solution or form an osazone, thereby showing that it contains no free aldehyde groups. It is lævorotatory and on hydrolysis with dilute acids it gives rise exclusively to glucose and malonic acid; at the same time the acidity of the material is doubled. From these and other considerations, it is concluded that the substance is a complex built up of units, each of which is a condensation product of two molecules of glucose with one molecule of malonic acid with the loss of two molecules of water, in which one carboxyl is free and the other in combination, and two aldehyde groups are linked in such a way as to destroy their aldehydic properties. Polysaccharides of this type, in which part of the simple hexose units is replaced by a simple organic acid, are very rare, and the only other well-authenticated example is, curiously enough, also of microbiological origin. This is the " soluble specific substance " from young cultures of *pneumococcus* which has been recently isolated by Heidelberger and Goebel[31] and shown to give rise to glucose and glucuronic acid on hydrolysis. The natural gums, *e.g.*, gum arabic, are of course of similar type, but in these cases the nature of the complex constituent acid has not been worked out.

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[26] J. H. Birkinshaw, A. C. Hetherington, and H. Raistrick, *Phil. Trans.*, 1930, **220**, Pt. 9.

[27] H. Raistrick and W. Young, *ibid.*, Pt. 10.

[28] *Idem, ibid.*

[29] J. H. Birkinshaw, J. H. V. Charles, and H. Raistrick, *ibid.*, Pt. 18.

[30] H. Raistrick and M. Rintoul, *ibid.*, Pt. 13.

Kojic Acid.—This acid was shown by T. Yabuta in 1924[32] to be 5-hydroxy-2-hydroxymethyl-γ-pyrone, and is characterised by the intense wine-red colour it gives with ferric chloride in dilutions of even 1 : 200,000. In ignorance of earlier work Raistrick and his co-workers[33] in 1923 found that the balance sheet of *A. parasiticus* showed that more than 19% of the sugar consumed was unaccounted for, and from this investigation rediscovered this acid, noted in Yabuta's paper. *A. flavus, effusus,* and *tamarii* also give this acid, which appears to be of diagnostic value, in that it justifies one in placing in the *flavus-oryzæ-tamarii* group of *Aspergilli* any species of this genus which, if cultured under certain specified conditions, gives rise to the typical kojic acid reaction, without, however, necessarily excluding from this group any *Aspergillus* which gives a negative reaction.

F. Traetta-Mosca[34] showed that the acid is produced from glycerol, sucrose, glucose and lævulose by a mould which he called *A. glaucus*, but which Raistrick and his co-workers believe to be a member of the *flavus-oryzæ* group. F. Challenger, L. Klein, and T. K. Walker[35] showed that it was produced by a mould they call *A. oryzæ diastase* from arabinose and xylose, and the list of precursors given by Raistrick and his co-workers includes all these substances together with lactose, galactose and mannitol. The latter workers point out that the idea originally held, that kojic acid ($C_6H_6O_4$) arises from glucose ($C_6H_{12}O_6$) by a simple oxidation and dehydration, offers no explanation of the formation of the acid from compounds containing less than six carbon atoms in the molecule, *e.g.*, xylose, arabinose, and glycerol. They think that either of the following explanations seems to offer a solution of the difficulty, but consider that there is at present no conclusive experimental evidence as to whether either is correct :—

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[31] *Ann. Reports*, 1927, **24**, 251.

[32] *J.*, 1924, **125**, 575.

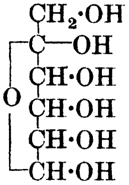
[33] J. H. Birkinshaw, J. H. V. Charles, C. H. Lilly, and H. Raistrick, *Phil. Trans.*, 1930, **220**, Pt. 7; J. H. Birkinshaw and H. Raistrick, *ibid.*, Pt. 8.

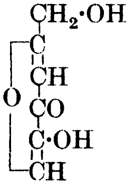
[34] *Gazzetta*, 1921, **51**, ii, 269; *A.*, 1922, i, 91.

[35] *J.*, 1929, 1498; *A.*, 1929, 1042.

(1) In common with some other types of fermentation, as shown for glycerol by Neuberg and his co-workers, acetaldehyde may be produced by the fungus from the carbon source supplied, whether this be a poly-, di-, or mono-saccharide, a pentose or a polyhydric alcohol. The acetaldehyde may then be condensed by a series of reactions to kojic acid. This explanation is apparently supported by the fact that it has been shown that all those fungi which produce kojic acid also produce at the same time ethyl alcohol, and hence, in passing, acetaldehyde.

(2) The source of carbon supplied, whatever its nature, may be first metabolised by the fungus into a reserve carbohydrate, which is later hydrolysed by the micro-organism, as occasion arises, into a mono-saccharide which in its turn gives rise to kojic acid. The close similarity between the amylene-oxide form of a 6-carbon sugar and kojic acid renders this a probable explanation, and it is further supported by the fact that various fungi are known to store reserve carbohydrates, and to utilise them later as occasion demands, *e.g.*, glycogen in yeast, trehalose in *A. niger*.





The view that the immediate precursor of the kojic acid is a 3-carbon compound is favoured by F. Challenger, L. Klein, and T. K. Walker, who cite as a parallel the production of citric acid from pentoses, and by A. Corbellini and B. Gregorini,[36] who consider that the pyrone nucleus is formed by synthesis from 3-carbon oxidation products of glycerol by a reaction analogous to that occurring with aldehydes under the action of carboligase.

New Phenolic Substances.—Using glucose as source of carbon and the carbon balance sheet as a guide to indicate the formation of "unaccounted carbon," Raistrick and his co-workers have isolated three new highly-coloured phenolic substances.

From certain species of *Citromyces* [37] they have obtained yields as high as 25% of the sugar fermented of a new yellow benzopyrone derivative having the formula $C_{14}H_{10}O_7,2H_2O$, which they have named citromycetin. It is a dihydroxy-carboxylic acid containing a benzopyrone nucleus, and from a study of its decomposition products it is considered to be (I).

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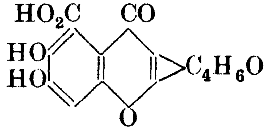
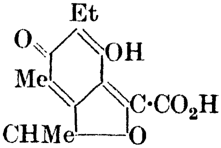
[36] *Gazzetta*, 1930, **60**, 244; *A.*, 959.

[37] A. C. Hetherington and H. Raistrick, *Phil. Trans.*, 1930, **220**, Pt. 11.

(I.)





(II.)

From *P. citrinum*, Thom,[38] and from no other species they have isolated a new yellow crystalline colouring matter having the empirical formula $C_{13}H_{14}O_5$ which they have named citrinin. From a study of its decomposition products F. P. Coyne, H. Raistrick, and R. Robinson[39] tentatively assign to this compound the formula (II). They call attention to the fact that this carbon skeleton contains two straight chains of 6 carbon atoms each, joined at their γ-positions by a thirteenth carbon atom.

A third coloured substance, which separates as purplish-black permanganate-like crystals of the formula $C_8H_8O_5$, was produced, together with much citric acid, by a strain of *Penicillium spinulosum*, Thom.[40] It is a dihydroxymethoxytoluquinone, and is the first recorded instance of the production from glucose by fungi of a quinone derivative. It appears fairly certain that the substance is a *p*-quinone, but the relative positions of the methyl, methoxy, and two hydroxyl groups in the quinonoid nucleus can only be finally settled by synthesis, as compounds of this type have not yet been described in the literature.

Perhaps the most interesting of the new products obtained from glucose is the new polybasic fatty acid given by *P. spiculisporum* Lehman.[41] It is the lactone of γ-hydroxy-$\beta\delta$-dicarboxypentadecoic acid (III), and its constitution has been proved in the following way. The substance is a dibasic acid and is stable towards acid. On hydrolysis with caustic soda it yields a tribasic acid (IV), which forms a monoacetyl derivative. The ease with which this tribasic acid reverts to the parent substance with loss of water on heating suggests that it is a γ-hydroxy-tricarboxylic acid. On fusion with potash the tribasic acid yields lauric acid (VI), succinic acid (VII) and carbon dioxide, and on oxidation with permanganate in acetone solution it gives a theoretical yield of a keto-acid shown by synthesis to be γ-ketopentadecoic acid (V).

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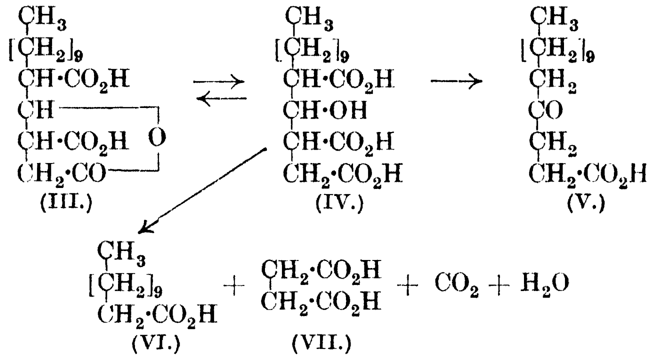
[38] A. C. Hetherington and H. Raistrick, *Phil. Trans.*, 1930, **220**, Pt. 14.

[39] *Ibid.*, Pt. 15.

[40] J. H. Birkinshaw and H. Raistrick, *ibid.*, Pt. 12.

[41] P. W. Clutterbuck, H. Raistrick, and M. Rintoul, *ibid.*, Pt. 16.



$$\underset{\text{(III.)}}{\begin{array}{l} CH_3 \\ [CH_2]_9 \\ CH\cdot CO_2H \\ CH\text{———}\rceil \\ CH\cdot CO_2H\ \ O \\ CH_2\cdot CO\text{——}\rfloor \end{array}} \rightleftarrows \underset{\text{(IV.)}}{\begin{array}{l} CH_3 \\ [CH_2]_9 \\ CH\cdot CO_2H \\ CH\cdot OH \\ CH\cdot CO_2H \\ CH_2\cdot CO_2H \end{array}} \longrightarrow \underset{\text{(V.)}}{\begin{array}{l} CH_3 \\ [CH_2]_9 \\ CH_2 \\ CO \\ CH_2 \\ CH_2\cdot CO_2H \end{array}}$$

$$\swarrow$$

$$\underset{\text{(VI.)}}{\begin{array}{l} CH_3 \\ [CH_2]_9 \\ CH_2\cdot CO_2H \end{array}} + \underset{\text{(VII.)}}{\begin{array}{l} CH_2\cdot CO_2H \\ CH_2\cdot CO_2H \end{array}} + CO_2 + H_2O$$

These results show that the tribasic acid (IV) is γ-hydroxy-$\beta\delta$-dicarboxypentadecoic acid, and that the parent substance (III) is its γ-lactone. It is interesting to note that γ-ketopentadecoic acid itself was isolated from the metabolism solution, so that we have here an undoubted instance of the production by a living organism of a fatty acid containing an odd number of carbon atoms. It is to be remembered, however, that this C_{15} acid and its dicarboxy-derivatives are not constituents of the mould " fat " but are excreted into the fermentation solution, so their discovery does not necessarily upset the view, now generally accepted, that natural fats contain only even-numbered carbon fatty acids.

The degradation of the lower fatty acids themselves by fungi has been recently investigated by T. K. Walker and his co-workers. *A. niger* was grown on an aqueous solution of the calcium salt of the fatty acid together with the requisite inorganic salts.[42] Calcium propionate was oxidised at the α-carbon atom, and lactic acid was always detected (thiophen test) before pyruvic acid (coloration given with benzenediazonium chloride in the presence of sodium acetate). Calcium *n*-butyrate, *n*-valerate and *iso*valerate gave the respective β-hydroxy-acid and β-keto-acid and methyl ketone successively, showing that β-oxidation had occurred in these cases.[43]

The precise mechanism of β-oxidation of the normal fatty acids *in vivo* is not yet known with certainty, previous experimental work indicating that the first product may be either a β-keto-acid, a β-hydroxy-acid or an $\alpha\beta$-unsaturated acid. All of these are equally easily oxidised by the liver and are interconvertible.[44]

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[42] T. K. Walker and P. D. Coppock, *J.*, 1928, 803; *A.*, 1928, 804.

[43] P. D. Coppock, V. Subramaniam, and T. K. Walker, *ibid.*, p. 1422; *A.*, 1928, 804.

[44] H. D. Dakin, *J. Biol. Chem.*, 1923, **56**, 43.

When *A. niger* was grown on calcium *n*-butyrate Walker and his co-workers could not detect crotonic acid in the culture medium, nor would the mould grow on calcium crotonate as sole source of carbon. They consider that their evidence points to the initial formation of a β-hydroxy-acid and its subsequent oxidation to the corresponding β-keto-acid. They therefore differ from W. N. Stokoe,[45] who considers that the β-keto-acid is the initial product.

The Chemistry of Plant Pathology.

Pressing problems of economic importance have led during recent years to a great increase in the amount of research devoted to plant pathology, but the mode of attack has been almost entirely biological and research on strict chemical lines has been rarely initiated and still more rarely successful. It is therefore noteworthy that the differences in susceptibility to a parasite of closely related plants have been definitely connected with the presence or absence of a chemical entity in the host.[46] Red and yellow varieties of the common onion (*Allium cepa*) are in general resistant to the diseases caused by the fungus *Colletotrichum circinans* (Berk), whereas the white varieties are susceptible. Investigations revealed that an aqueous extract of the dry outer pigmented scales causes rupturing or abnormal germination of the spores and retards the growth of the mycelium of the fungus, whereas a similar extract from the dry outer white scales is not endowed with this property. Fractionation of the former extract led to the isolation of protocatechuic acid, which was found to be as toxic in dilutions of 1 part to 3000 parts of water as the original extract itself. The mode of preparation of the extract (digestion with 20 parts of water at 30° for 2 hours) and the chemical methods used in the fractionation exclude the possibility of the acid having arisen by decomposition from quercetin, which Perkin [47] showed was present in pigmented onion scales.

The spike disease of Sandal (*Santalum album*, Linn.) has been investigated by M. Sreenivasaya [48] and his colleagues. They find that the diseased leaves have a higher content of reducing sugars, total carbohydrates, and both total and soluble nitrogen than healthy ones, and the sap has a definitely higher diastatic activity. Furthermore they state that mannitol can be isolated from diseased leaves, whereas it appears to be absent in healthy ones.[49]

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[45] *Ann. Reports*, 1929, **26**, 210.

[46] K. P. Link, H. R. Angel, and J. C. Walker, *J. Biol. Chem.*, 1929, **84**, 719; *A.*, 1929, 122; J. C. Walker, K. P. Link, and H. R. Angel, *Proc. Nat. Acad. Sci.*, 1929, **15**, 845; *A.*, 1929, 262; H. R. Angel, J. C. Walker, and K. P. Link, *Phytopath.*, 1930, **20**, 431; *A.*, 1224.

[47] A. G. Perkin and J. Hummel, *J.*, 1896, **69**, 1295.

[48] *J. Indian Inst. Sci.*, 1928, **11A**, 23, 97; 1929, **12A**, 153; *A.*, 1928, 804, 1291; 1930, 385.

A. A. Dunlap [50] has studied the virus diseases of plants, and suggests that they may be divided into two classes, mosaic diseases and yellows diseases, according to the effect of the disease upon the total nitrogen and total carbohydrate contents of the leaves of the host plants. Mosaic disease caused an increase of nitrogen and a decrease of carbohydrate, whereas yellows disease brought about the reverse effect. His results are in general agreement with those of earlier workers; E. G. Campbell,[51] for instance, found that leaf-roll disease of potato is accompanied by increase of carbohydrate, and R. H. True and L. A. Hawkins [52] found an increase of carbohydrate, and S. L. Jodidi [53] a decrease of total nitrogen, in blight disease of spinach. Dunlap considers that the latter should be classified as a yellows and not as a mosaic disease. Again, in fruits, A. S. Horne and F. G. Gregory [54] find that resistance to disease in apples is associated with high acidity, high potassium and low nitrogen, although the converse may also be true.

Turning to the question of inorganic deficiency and plant diseases, it is of course well known that lack of certain essential elements such as iron, potassium, and calcium brings about leaf chlorosis. But during recent years it has become increasingly evident, chiefly through the work of J. B. Orr and his school at Aberdeen,[55] that inorganic elements play a fundamental part in determining the nutritive value of pasture grasses. Deficiencies may occur which, though not so marked as to cause gross signs of disease, may yet limit the rate of growth and the rate of productivity. Furthermore these smaller deficiencies may adversely affect the " constitution " of the animal, rendering it more susceptible to some disease of bacterial origin.

R. Adam [56] and his colleagues have carried out an interesting investigation into the bactericidal action of a number of cyclic and straight-chain fatty acids, which they have synthesised from appropriate alkyl halides by the malonic ester condensation.

The six different isomeric series of acids containing *cyclo*hexyl groups,

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[49] *Nature*, 1930, **126**, 438; *A.*, 1483.

[50] *Amer. J. Bot.*, 1930, **17**, 348.

[51] *Phytopath.*, 1925, **15**, 427.

[52] *J. Agric. Res.*, 1918, **15**, 381.

[53] *J. Amer. Chem. Soc.*, 1920, **42**, 1061, 1885; *A.*, 1920, i, 586.

[54] *Proc. Roy. Soc.*, 1928, [*B*], **102**, 444.

[55] Reviewed by J. B. Orr, " Minerals in Pasture," London, 1929.

[56] See W. M. Stanley, M. S. Jay, and R. Adams, *J. Amer. Chem. Soc.*, 1929, **1**, 1261; *A.*, 1929, 676, in which reference is given to a series of 15 papers.

$C_6H_{11}\cdot[CH_2]_x\cdot CO_2H$, $C_6H_{11}\cdot CHR\cdot CO_2H$, $C_6H_{11}\cdot CH_2\cdot CHR\cdot CO_2H$, $C_6H_{11}\cdot[CH_2]_2\cdot CHR\cdot CO_2H$, $C_6H_{11}\cdot[CH_2]_3\cdot CHR\cdot CO_2H$, and $C_6H_{11}\cdot[CH_2]_4\cdot CHR\cdot CO_2H$, were found to possess high bactericidal action *in vitro* to *B. lepræ.* The effect increased with increase of molecular weight of the alkyl group, and was most potent when the acids had 16—18 carbon atoms. Further, those acids with the carboxyl group at the end of the chain were not nearly as effective as the isomerides with the carboxyl near the ring. As chaulmoogric and hydnocarpic acids both contain the Δ^2-*cyclo*pentenyl group, it seemed possible that a ring was necessary for bactericidal action; accordingly a series of acids of the general formula $RCH(CO_2H)R'$, in which R is a *cyclo*pentyl, *cyclo*pentenyl or *cyclo*propyl group, or one of these groups substituted in the ω-position of the alkyl group, and R′ is an alkyl group, was prepared and studied. The results indicated that there was no very marked difference between the acids containing the 3-, 5- or 6-membered rings, and that those with 16—18 carbon atoms were again the most effective. Finally a number of isomeric octadecoic and hexadecoic acids, which included a complete series of compounds with chains of seventeen and fifteen carbon atoms, and a carboxyl group substituted in every possible position, were prepared. The results with these acids showed conclusively that no ring was necessary for bactericidal action, and again it was found that the terminal carboxyl group was the least effective. Adams and his co-workers conclude from their studies that the effect of these acids towards *B. lepræ* and other acid-fast bacteria can hardly be attributed to the chemical specificity of the individual acids, and is probably due to a combination of physical properties common to many of them.

J. M. Schaeffer and F. W. Tilley[57] have investigated many isomeric alcohols in a similar way and find that those with the longest straight chains or phenols having the longest straight chain in the para-position are the most efficacious germicides. The coefficients of *cyclo*hexanol and of methyl*cyclo*hexanols are about half as great as those of phenol and the corresponding cresols.

The efficacy as contact insecticides of the *n*-fatty acids from formic to stearic, and of their sodium and ammonium salts and methyl esters, has been investigated by F. Tattersfield and C. T. Gimingham.[58] The toxicity to *Aphis rumicis* L. of the acids from acetic to undecoic rises with increase of molecular weight. The salts and esters were in general less toxic than the acids, but showed a similar rise with increase of molecular weight. The authors suggest

[57] *J. Bact.*, 1927, **14**, 259; *A.*, 1928, 795.

[58] *Ann. Applied Biol.*, 1927, **14**, 331.

that the toxicity of these acids is bound up in some way with water-solubility relationships.

Nitrogenous Metabolism in the Plant.

During the past year several interesting papers dealing with the nitrogen question in plants have been published. Many of these emanate from Agricultural Stations, and much of the matter contained therein, although of great agricultural or horticultural interest, does not find a place in a Report devoted chiefly to progress on the chemical side. In addition, certain papers of fundamental importance published in a new journal, *Planta*, during the past four years—to which the attention of the Reporter has only recently been directed—fall to be discussed this year.

Nitrogen Fixation by Bacteria.—Recent work by D. Burk on the metabolism of *Azotobacter* has led him to question the validity of the theory, now generally held, that the first stage in the fixation of atmospheric nitrogen is the production of ammonia. He has used the manometric micro-methods for the study of cell-metabolism devised by O. Warburg.[59] He has shown—partly in collaboration with O. Meyerhof [60]—that *Azotobacter* behaves uniquely towards oxygen gas. Its rate of oxygen consumption and its efficiency of nitrogen fixation are markedly conditioned by oxygen pressure in a manner characteristic of no other living organism. (1) The rate of respiration (measured directly by oxygen consumption) attains a maximum at 0·15 atmosphere, diminishing rapidly at both higher and lower pressures, being only one-third as great at 0·005 and 1·0 atmosphere. (2) The decrease in rate of respiration between 0·2 and 1·0 atmosphere of oxygen is linear; this is true whether the complementary gas making the total pressure up to one atmosphere is nitrogen or hydrogen. (3) In the absence of free or fixed nitrogen, which would permit growth, the rates of respiration are independent of time at any given oxygen pressure, except in the high region of 1 atmosphere, when they fall off with time. (4) In a young culture the rate of respiration is enormously high, 2000 c. mm. of oxygen per mg. of dry matter per hour, or about three times its own dry weight of glucose. In contrast it may be noted that O. Warburg's value for baker's yeast is only 75 c. mm. and that the rate of respiration is independent of oxygen pressure between 0·03 and 0·97 atmosphere. (5) The rate of nitrogen fixation attains a maximum at 0·4 atmosphere of oxygen, and is only one-third to one-sixth as great at 0·008 and 0·21 atmosphere. (6) The most important influence of oxygen pressure, however, is upon the efficiency ratio, nitrogen fixed/oxygen consumed, which increases some ten- to twenty-fold between 0·21 and 0·01 atmosphere.

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[59] "Über den Stoffwechsel der Tumaren," 1926, p. 1—11.

[60] *Z. physiol. Chem.*, 1928, **139**, 117; *A.*, 1929, 473; *J. Physical Chem.*, 1930, **34**, 1174, 1195; *A.*, 1068.

Burk admits that it is logical to suppose that these unusual metabolic properties are either the cause or the result of the similarly exceptional ability of *Azotobacter* to fix nitrogen, and that any theory of the chemical or catalytic mechanism of nitrogen fixation must provide an explanation of them. This type of reasoning, for instance, has been applied by certain workers recently to the behaviour of certain strains of *Azotobacter;* [61] because ammonia was found in the culture fluid, it was considered to prove that ammonia was concerned in nitrogen fixation. He does not think that such reasoning is valid and recalls Winogradsky's [62] original findings that the ordinary metabolism and nitrogen fixation of these organisms are two distinct phenomena. The strains of *Azotobacter* used by these workers produce ammonia extracellularly whether growing in either nitrogen gas or nitrate, and therefore there is no proof that ammonia is involved in their mechanism of fixation; indeed, since nitrates and nitrites are reduced vigorously to ammonia, it is equally likely that the mechanism involves, rather than precludes, the formation of nitrogen-oxygen compounds such as nitrates. Burk's strains of *Azotobacter* produce neither ammonia nor nitrates extracellularly during fixation, nor ammonia when growing on nitrates, and he does not think that they can possess a different method of fixation.

Burk has so far established certain facts concerning the mechanism of fixation which are free from the above logical inconsistency. (1) At 0·2 atmosphere of oxygen, nitrogen is fixed at an appreciable rate only above 0·05 atmosphere, and tends to reach a maximum value at about 5 to 10 atmospheres. (2) The efficiency of nitrogen fixation increases markedly with the rate of fixation. (3) All the unique oxygen pressure functions described above obtain in cultures growing on fixed nitrogen, and therefore offer no indication as to the nature of the chemical mechanism of fixation.[63] (4) Humic acid, which greatly accelerates nitrogen fixation, is not directly concerned with the mechanism of fixation but is a growth stimulant. (5) The failure of legume bacteria to fix nitrogen in the absence of the host plant has been confirmed by gasometric studies under a variety of pressures of nitrogen, hydrogen or oxygen between 0 and 1 atmosphere. (6) The view of previous workers is supported and enlarged upon, that fixation is a function resorted to only in the absence of sufficiently available fixed nitrogen.

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[61] S. Kostychew, A. Ryskaltschuk, and O. Schwezowa, *Z. physiol. Chem.*, 1926, **134**, 1.

[62] *Compt. rend.*, 1893, **116**, 1385; *Arch. Sci. Biol. St. Petersburg*, 1894—5, **3**, 297.

[63] D. Burk and H. Lineweaver, *J. Bact.*, 1930, **19**, 389; *A.*, 1219.

D. W. Cutler[64] records a new group of organisms distinct from *Nitrosomonas* and *Nitrosococcus*, which produce nitrite from ammonia.

Nitrate Reduction in Plant Roots.—The presence of small amounts of nitrate in green leaves has led to the view that the synthesis of organic from inorganic nitrogen generally takes place in these organs. An interesting paper by G. T. Nightingale and L. G. Schermerhorn[65] shows that active reduction of nitrate to ammonia may take place in the root system. When the asparagus plant is in a condition of active vegetative growth of tops, nitrates can be found only in the fibrous roots. In a plant lacking nitrates in its tissue and nutrient medium, but containing reserve carbohydrate within its roots, the external supply of nitrate leads to the production of nitrites and ammonia in the fibrous roots only and not in the storage roots. At the same time asparagine and amino-acids appear in these organs in considerable quantities and the amount of reserve carbohydrate is reduced. The transformation of nitrates is most rapid from 20° to 30°, and is very slow at 10°. The storage roots and actively growing tops of the asparagus plant apparently may assimilate nitrates, but rather seldom have an opportunity to do so because nitrates are transformed to organic nitrogen in the fibrous roots before reaching other organs of the plant. If, however, the temperature is 10° or lower, nitrates may be translocated to other parts of the plant. Later, with a rise of temperature, nitrates are rapidly assimilated by and disappear from both the storage roots and the actively growing tops and are then found again only in the fibrous roots.

A similar transformation of nitrate to organic nitrogen was observed by G. T. Nightingale and W. R. Robbins[66] in the fine fibrous roots of the paper-white narcissus (*Polyanthus narcissus*), and W. Thomas[67] concludes from his research on the nitrogen metabolism in *Pyrens malus*, L., that the transformation takes place for the most part in the roots.

Nitrogenous Metabolism in Underground Storage Organs.—R. Grüntuch[68] has reviewed what little earlier work there is on this subject and has carried out a long series of experiments with the underground storage organs of many plants, chiefly with *Solanum*

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[64] *Nature*, 1930, **125**, 168; *A.*, 376.

[65] *N. J. Agric. Exp. Sta. Bull.*, 1928, No. 476; *A.*, 507.

[66] *Ibid.*, 1928, No. 472; *A.*, 1929, 612.

[67] *Science*, 1927, **66**, 115; compare *Ann. Reports*, 1927, **24**, 230.

[68] *Planta*, 1929, **7**, 382.

tuberosum, *Helianthus tuberosus*, *Dahlia variabilis*, and *Asparagus officinalis*. He finds, as one would expect, that the total nitrogen in these organs varies greatly, not only in different plants, but also in the same plant at different stages of growth. In spite of this the ratio of protein/soluble nitrogen remains fairly constant. Grüntuch concludes that the metabolism of these storage organs remains obscure, and is not to be compared with that of the ripening seed.[69] If nitrates (which Grüntuch has not determined) are transformed in the fibrous root, as discussed above, and do not accumulate in the storage organs, then the soluble nitrogen is presumably all organic nitrogen, and it is possible that we are dealing here with some "mass-action" relation between protein and soluble nitrogen similar to that postulated by L. R. Bishop[70] in the development of the reserve proteins in the barley grain.

The Rôle of Ammonia in Plant Metabolism.—In a series of papers published during the last thirty years D. Prianischnikov has developed a theory, now generally accepted, that ammonia is the "alpha and omega" of nitrogen metabolism in the plant. Ammonia, however, was never stored as such in the plant but was metabolised to "amides" (asparagine and glutamine). If the carbohydrate reserve in the plant was insufficient for this purpose, the plant rapidly died. He considered, therefore, that ammonia was a plant poison, and that "amides" were an innocuous form of ammonia storage.[71]

In a brilliant series of papers published during the last three years W. Ruhland and K. Wetzel have shown that in certain types of plant—those with a very acid sap—these conditions do not hold, and that an accumulation of ammonia (as salts, not free) can occur to an extent hitherto considered improbable. Within the limits of this Report it is possible to give only a brief outline of the more important of their results in as far as they relate to the metabolism of nitrogen.

The high sap acidity (p_H 1·54—1·56) of leaves of *Begonia semperflorens* suggested that they might be used for investigations on the metabolism of organic acids.[72] The following differences between these leaves and those of normal acidity (p_H 5—6·5) were observed.

(1) If the leaves were kept in the dark, the respiratory quotient rose from an initial 1·1 to 1·47—1·85 at the end of 3 days. Normal leaves showed a fall below 1.

(2) They contained 20% of their dry weight as oxalic acid.

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[69] F. Czapek, "Biochemie der Pflanzen," II, 279.

[70] *Ann. Reports*, 1929, **26**, 219.

[71] *Biochem. Z.*, 1928, **193**, 211; 1929, **207**, 341; *A.*, 1928, 562; 1929, 728; compare M. E. Robinson, *New Phyt.*, 1929, **28**, 117.

[72] W. Ruhland and K. Wetzel, *Planta*, 1926, **1**, 558; H. Ullrich, *ibid.*, p. 565.

(3) They contained 5—10 times the normal preformed ammonia, and the value increased threefold during the day. Whereas in normal leaves the value (soluble N — ammonia N)/ammonia N was usually about 50, in begonia it was only 2—3. If the leaves were kept in the dark at 28—35° to bring about protein decomposition, the ammonia content rose enormously—in 106 hours to 30% of the total nitrogen, while the small initial amount of " amide " nitrogen disappeared. The deamination was accompanied by a parallel increase in oxalic acid (the p_H of the sap decreased to 1·3) so that the ammonia was always present as ammonium oxalate, and at no time was free ammonia poisoning possible. In normal plants, of course, the " amide " nitrogen increases in the dark, the ammonia remaining more or less stationary. Ruhland and Wetzel therefore consider that plants can be separated into two physiological types—" amide " plants and " ammonia " (or " acid ") plants.

In further illustration of this new important observation may be cited certain of their results with rhubarb (*Rheum hybridum hort*).[73] The rhizome, which has only a slight acid reaction, contains " amide " nitrogen (20% of the total soluble nitrogen), much amino-nitrogen (50% of the total), and only traces of ammonia. The stalks of the very young leaves synthesise protein rapidly from the amino-acids and amides translocated from the rhizome. This ceases as the leaves open, and a little later, when the stalks are 15 cm. long, strong deamination takes place. The fully grown stalks contain some 62% of their total nitrogen as ammonia, and if they are kept in the dark this value may rise to 72%. Parallel with the production of ammonia during growth is the production of (chiefly) malic and succinic acids, which give place slowly, as the stalk ages, to oxalic acid; so that free ammonia poisoning is again prevented. Both *l*-malic and *dl*-malic acids are found and it is considered that the inactive acid has been translocated from the rhizome, in which this modification only is found, and that the active acid has arisen by deamination of amino-acids, since the relative concentrations of ammonia and this active acid are nearly 1 : 1. It is interesting to note that the leaf laminæ, which are much less acid than the stalks, contain the usual amount of protein (88—91% of the total nitrogen) and only traces of ammonia. That " amide " plants can, in an emergency, mobilise ammonia is shown by some results of D. Prianischnikov,[74] in which the roots of certain embryos, after being dipped in acid, gave off ammonia and, to a certain extent, neutralised the acid.

Ruhland and Wetzel call attention to the close similarity between the metabolism of these " acid " plants and that of *Aspergillus niger* growing on peptone,[75] in which 78% of the soluble nitrogen is converted into ammonia and there is an equivalent production of oxalic acid. Another interesting parallel is the production of *dl*-malic and *l*-malic acid during the metabolism of rhubarb stalks and the production of both these acids by *A. niger* (p. 233).

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[73] W. Ruhland and K. Wetzel, *Planta*, 1927, **3**, 765; K. Wetzel, *ibid.*, 1927, **4**, 476.

[74] *Biochem. Z.*, 1928, **193**, 211; *A.*, 1928, 562.

Synthesis of Protein in Green Leaves.—J. Björkstén [76] has put forward some interesting views on the intermediary products of synthesis in leaves which are based on an entirely new method of experimentation. The intercellular spaces of leaves of wheat seedlings suffering from nitrogen starvation were injected with various nutrient solutions by the evacuation method. The protein nitrogen (in mg. per 1 g. of dry leaf) was then compared every hour for 6 hours with that of control leaves. As an efficient control source of nitrogen, $0{\cdot}01M$-urea was used. Injection with hydrogen peroxide greatly increased the production of carbon dioxide, but protein synthesis went on normally. Changing the acidity of the solution between p_H 4 and p_H 8, or the osmotic pressure by adding potassium, sodium, or chlorine ions, again had no effect on protein synthesis. As sources of carbon for protein synthesis, none of the simple aliphatic or hydroxy-acids was of use. Pyruvic acid (but none of its homologues) was, however, readily utilised, and as there was no increase in carbon dioxide formation it would appear that the acid did not undergo decarboxylation. Of the sugars tried, only glucose was utilised. Aliphatic amines, amino-acids, and ammonium salts of aliphatic organic acids were good sources of nitrogen supply, nitrates less so, and cyclic products were not utilised at all. Hydrogen cyanide and nitrites, which Traub [77] considered might be precursors of amino-acids, were not used as sources of nitrogen.

Björkstén discusses the various hypotheses that have been advanced to account for the synthesis of amino-acids in the light of his own results, and puts forward a new suggestion that the simplest building stone for protein synthesis is α-aminoacrylic acid, formed by the condensation of enolic pyruvic acid and ammonia.

In a second paper J. Björkstén and I. Himberg [78] discuss certain aspects of the rôle of ammonia in protein synthesis. Injection of etiolated wheat leaves with urea, acetamide, and butyramide leads to protein synthesis but no increase in free ammonia. Under ether narcosis, injection of urea leads to an increase of free ammonia, but no such increase is produced by acetamide and butyramide. As far as is known at present, there is no enzyme which will hydrolyse these amides, whereas, of course, urea is readily broken down by urease. They conclude, therefore, that ammonia plays no direct rôle in protein synthesis from these amides, and postulate a mechanism by means of which the amides are condensed directly with pyruvic acid to give α-aminoacrylic acid.

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[75] W. Butkevitsch, *Biochem. Z.*, 1922, **129**, 445.

[76] *Ibid.*, 1930, **225**, 1; *A.*, 1482.

[77] Compare M. E. Robinson, *Biol. Reviews*, 1930, **5**, 126.

[78] *Ibid.*, 1930, **225**, 441.

They consider that urea can also condense directly with enolised pyruvic acid to form α-aminoacrylic acid, which is of interest because G. Klein [79] has recently asserted that the major part of the urea in plants—and its wide distribution in small amounts is well known—is not free, but bound with formaldehyde or acetaldehyde as a ureide.

Nitrogen Exchange in Plants.—Certain aspects of this problem were discussed in last year's Report.[80] During this year several papers have appeared, some of which favour the view that amides are concerned chiefly with storage, and that organic nitrogen is transported as amino-acids. E. J. Maskell and T. G. Mason [81] in continuation of their researches on the cotton plant have traced the movements of nitrogen in the boll, and conclude from a study of the nitrogen gradients into the boll during growth that the organic nitrogen enters from the sieve-tubes as " residual " rather than as " amide " nitrogen. H. Engel [82] has made some interesting observations on plants suffering from nitrogen starvation. Cut shoots were kept for some weeks with their ends in distilled water, and the flow of nitrogen between the older fully grown and the young developing leaves was observed. The older leaves suffered much protein decomposition, but the soluble nitrogen was decreased also, showing that the products of decomposition had been translocated. Engel discusses the variations found in the ammonia-, amide-, and what he refers to as amino-nitrogen, and concludes that the nitrogen from the older leaves has been translocated to the growing parts as amino-nitrogen. Single leaves were used in some experiments, so the material available for micro-chemical analysis was necessarily limited. His value for amino-nitrogen (total soluble N—ammonia N — twice the amide N) is open to criticism.[83]

K. Mothes [84] has made somewhat similar experiments. Cut tobacco plants were kept for 5—6 weeks in air that was 70% saturated. The older leaves withered and lost the major part of their protein, while the young growing leaves were still green and turgid and were actively synthesising protein. His analyses led him to the conclusion that the nitrogen was transported as amides from the old leaves to the younger. That the protein of old leaves—even in the presence of abundant carbohydrate—is more labile than that of young leaves was shown by K. Mothes in an earlier paper,[85] so that H. Engel's assumption that the nitrogen starvation leads to the protein breakdown in his older leaves does not necessarily follow. H. L. Newby and W. H. Pearsall [86] show that as the leaves of the vine and rhubarb become old the ratio of the protein to non-protein nitrogen decreases, as also does the acidity of the sap.

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[79] *Z. Pflanz. Düng.*, 1928, **12 A**, 390; *Abstracts of Communications, 5th International Congress of Botany, Cambridge*, 1930.

[80] *Ann. Reports*, 1929, **26**, 215.

[81] *Ann. Bot.*, 1930, **46**, 657; *A.*, 1323.

[82] *Planta*, 1929, **7**, 133.

[83] Compare H. B. Vickery, *Ann. Reports*, 1929, **26**, 212.

[84] *Ber. deut. Bot. Ges.*, 1928, **46**, 591.

A study of the soluble nitrogen in the leaves of the soya bean during development has been made by J. E. Webster,[87] and of the seasonal variations in the protein and soluble nitrogen in the mature leaves of three evergreen plants by H. Sattler.[88]

Plant Bases and Alkaloids.—Very little information on the metabolism of these substances in the plant is available, and there has been during the past two years a welcome increase of research devoted to the subject. G. Klein and M. Steiner [89] have investigated about 100 species of plant. All of them contained ammonia, and about 40 contained volatile amines. Methyl-, dimethyl-, trimethyl-, *iso*amyl-, and *iso*butyl-amine were identified by microscopic methods based on experiments with synthetic products. The amounts present ranged from 0·0005 mg.—0·2 mg. per 100 g. of fresh leaves. The authors consider that these volatile products are used to attract insects, and that they may be used as a basis for the systematic classification of plants. R. Kapeller-Adler and T. Csató find methylamine and trimethylamine in sea-weed.[90]

T. Weevers [91] has investigated the metabolism of caffeine and theobromine of several plants. They are found in the wood, underground organs, and especially in leaves. The amount in the last decreases as the leaf ages and disappears before it dies. Weevers considers that when this happens the bases are not translocated as such, but undergo degradation in the same way as protein. Excised leaves of *Ilex paraguariensis* [92] St. Hill show an increase of caffeine in daylight and a decrease if kept in the dark. Excised leaves of the tea plant, when kept in water, accumulate xanthine equivalent to 30% of the decomposed protein, an amount too large to permit the assumption that it has its origin in the leaf nucleo-protein. He considers that xanthine and its derivatives are storage products, and that their nitrogen can be utilised when occasion arises for protein synthesis.

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[85] *Planta*, 1926, **1**, 472. [86] *Proc. Leeds Phil. Lit. Soc.*, 1930, Section 2, 81.

[87] *Plant Physiol.*, 1928, **3**, 31; *A.*, 1929, 612.

[88] *Planta*, 1929, **9**, 315. [89] *Jahrb. wiss. Bot.*, 1928, **68**, 602.

[90] *Biochem. Z.*, 1930, **224**, 378; *A.*, 1484.

[91] *Arch. néerland. Sci.*, 1930, **VII B**, **5**, 111.

[92] *Proc. Acad. Sci. Amsterdam*, 1929, **32**, 281.

The position with regard to alkaloids is not yet so clearly defined. It will be recalled that Pictet considered them to be secondary products formed by the plant to remove poisonous primary products of metabolism. T. Weevers and H. D. van Oort [93] draw no definite conclusions from their experiments with the leaves of *Cinchona succirubia*, Pavon. K. Mothes [94] shows that there is a small gradual increase in nicotine as the leaves of the tobacco plant develop, but the connexion, if any, between the synthesis of nicotine and protein metabolism is not clear.

K. Mothes [95] has also investigated the metabolism of arginine in *Pinus spinea.* The base was estimated as flavianate after preliminary precipitation with phosphotungstic acid. In view of Vickery's [96] results on the composition of the basic fraction from alfalfa—which contained but very small amounts of arginine and consisted chiefly of basic compounds of undetermined composition (some of which may be precipitated by flavianic acid)—it seems to the Reporter that this method of analysis is unsound.

It is interesting to note that a new base closely allied to arginine has been isolated by M. Wade [97] from the press juice of the watermelon (*Citrullus vulgaris*). Its constitution, α-amino-δ-carbamidovaleric acid, $NH_2{\cdot}CO{\cdot}NH{\cdot}[CH_2]_3{\cdot}CH(NH_2){\cdot}CO_2H$, has been confirmed by synthesis from ornithine, by way of dibenzoylornithine, δ-amino-α-benzamidovaleric acid, and δ-carbamido-α-benzamidovaleric acid.

*Carbohydrate Constituents of Plant Tissue.**

The structure of pectic acid, which is generally accepted as the basis of all pectic substances, still provokes some discussion. The formula of Nanji, Paton, and Ling,[98] in which pectic acid is regarded as composed of 4 molecules of galacturonic acid, 1 molecule of galactose, and 1 molecule of arabinose combined in a hexa-ring, has been questioned by S. T. Henderson,[99] who obtained from flax a product having the composition of a galactose-tetragalacturonic acid (*i.e.*, containing no arabinose) and possessing all the properties of pectic acid. F. W. Norris [1] considers that the pectic acid of flax is of the normal type, as indicated by the furfural and " uronic anhydride " content. Ehrlich [2] still describes as " pectic acid " a water-soluble compound having the formula $C_{41}H_{60}O_{36}$, formed by the loss of 9 molecules of water from 4 molecules of galacturonic acid, 1 molecule of galactose, 1 molecule of arabinose, 2 molecules of acetic acid, and 2 molecules of methyl alcohol. This product was obtained in the form of a calcium magnesium salt, in association with an araban, by hot-water extraction of beetroot residues. The presence of methyl alcohol residues, and the solubility of the substance in water, seem to indicate that it is actually an intermediate between the completely demethoxylated, insoluble pectic acid ($C_{35}H_{50}O_{33}$) of other workers and " soluble pectin " (containing 4 methoxy-groups). The presence of acetic acid in the molecule has not been accepted by other workers.

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[93] *Proc. Acad. Sci. Amsterdam*, 1929, **32**, p. 1.

[94] *Planta*, 1928, **5**, 563; *Apoth.-Ztg.*, 1930, **13**, 3.

[95] *Planta*, 1929, **7**, 585.

[96] *Ann. Reports*, 1929, **26**, 212.

[97] *Proc. Imp. Acad. Tokyo*, 1930, **6**, 15; *Biochem. Z.*, 1930, **224**, 420; *A.*, 1224.

[98] *J. Soc. Chem. Ind.*, 1925, **44**, 253T.

[99] *J.*, 1928, 2117; *A.*, 1928, 1119.

* The Reporter gratefully acknowledges assistance from Dr. H. W. Buston in the preparation of this section.

J. R. Bowman and R. B. McKinnis [3] obtained from oranges an arabinogalacturonic acid, and by a similar process from apples a digalacturonic acid. These they regard as the nuclear units of the respective pectins. They suggest that the digalacturonic acid undergoes transition in nature to arabinogalacturonic acid (and possibly to arabinose), and that pectins contain these acids in varying proportions.

Although the ring formula for pectic acid is now widely accepted, the relation between this acid and " soluble pectin " still presents certain unexplained aspects. The action of weak alkali on pectin consists mainly in a removal of the methyl ester groups, the final product being the insoluble, completely demethoxylated pectic acid. It has been pointed out, however,[4] that pectic acid and methyl alcohol are not the sole products of the reaction, small amounts of a hemicellulose being invariably produced, a fact not accounted for by a simple saponification.

The results of E. J. Candlin and S. B. Schryver [5] may in part explain this. By the action of sodium hydroxide solution (0·5—4%) at temperatures between 37° and 100°, pectic acid was shown to undergo rapid decarboxylation, yielding products of a low " uronic anhydride " content—20% instead of 70% in the case of onion pectic acid. These products were shown to resemble the hemicelluloses in many of their properties. A similar decarboxylation was demonstrated by F. V. Linggood,[6] by heating pectic acid with water under pressure. About 12% of the pectic acid was accounted for as hemicellulose, the remainder being present possibly as degradation products of sugars. Since the pectins and the hemicelluloses have been proved to be closely related, the term " polyuronide " has been proposed to include both classes.

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[1] *Biochem. J.*, 1929, **23**, 195; *A.*, 1929, 729.

[2] F. Ehrlich and F. Schubert, *Ber.*, 1929, **62**, [*B*], 1974; *A.*, 1929, 1273.

[3] *J. Amer. Chem. Soc.*, 1930, **52**, 1209; *A.*, 746.

[4] F. W. Norris, *Biochem. J.*, 1925, **19**, 676; *A.*, 1925, i, 1226.

[5] *Proc. Roy. Soc.*, 1928, [*B*], **103**, 365; *A.*, 1928, 1162.

[6] *Biochem. J.*, 1930, **24**, 262; *A.*, 824.

An investigation on the hydrolysis of pectin by alkali has been made by A. G. Norman and J. T. Martin,[7] in an attempt to determine the mode of linkage between the individual members of the pectic acid ring. They pointed out that the pectin ring was extremely susceptible to attack by weak alkali (*e.g.*, 0·2% solution at 100°), indicating that the linkages between the units are probably unlike those found in other polysaccharides such as cellulose and starch. They found that rupture of the ring proceeded more rapidly than apparent decarboxylation, and criticised the conclusions drawn by Candlin and Schryver, since they were able to show that substances other than hemicelluloses and uronic acids were formed, and were capable of yielding large amounts of carbon dioxide with boiling hydrochloric acid.

Work on somewhat similar lines was carried out by A. G. Norman and F. W. Norris,[8] who studied the oxidation of pectic acid by Fenton's reagent. Pectic acid they proved to be readily oxidised, giving complex mixtures containing galactose and galacturonic acid residues. Their products strongly resembled the hemicelluloses, and the authors put forward the suggestion that, in nature, the latter may arise from the pectins by prolonged mild oxidation, rather than by decarboxylation. Certain of the gums have been shown to contain uronic acid residues, and may be formed similarly.[9]

Attention has often been directed to the fact that tissues rich in pectin are poor in lignin, and vice versa, and the suggestion has been made that pectin is the precursor of lignin. No practical evidence has been put forward in support of this view.

While evidence has been furnished that the hemicelluloses are related to the pectins in that they are based on conjugated sugar and sugar acid residues, their structure remains undecided. F. W. Norris and I. A. Preece [10] have isolated five types of hemicellulose from non-lignified tissues (wheat bran, maize cobs). Of these, hemicellulose A was precipitated from the caustic soda extract of the tissue on neutralisation with acetic acid; hemicellulose B, by the subsequent addition of a half-volume of acetone; and hemicellulose C by excess of acetone. B and C were subdivided into fractions B1 and C1 by precipitation with Fehling's solution, B2 and C2 remaining in the respective filtrates. Of these products, A was hydrolysed to xylose; B2 to glucose only; B1 and C1 gave varying amounts of xylose, methylpentose, and a uronic acid; C2 gave arabinose, methylpentose, and uronic acid. The uronic acid present was probably glycuronic acid. From a consideration of the amounts of pentose, etc., obtained, the hemicellulose molecule is evidently one of considerable complexity, B1 having a minimum molecular weight of 6500.

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[7] *Biochem. J.*, 1930, **24**, 649; *A.*, 966. [8] *Ibid.*, p. 402; *A.*, 824.

[9] A. G. Norman, *ibid.*, 1929, **23**, 524; *A.*, 1929, 856.

[10] *Ibid.*, 1930, **24**, 59; *A.*, 383; I. A. Preece, *ibid.*, p. 973; *A.*, 1325.

In the case of the hemicelluloses from lignified tissue, M. H. O'Dwyer[11] showed that the methoxyl groups were of two types, one of which was extremely resistant to hydrolysis, and therefore was not an ester group. The hemicelluloses derived from timber are by no means of the same structure as those from non-lignified tissues, although extracted by similar means. The products from wood have, in general, a much higher uronic anyhdride content and are apparently more complex in nature. Other tissues (*e.g.*, flax) yield hemicelluloses containing varying proportions of uronic anhydride residues.[99]

Certain substances intermediate between the pectic substances and the simple sugar acids have been isolated and studied, notably by F. Ehrlich.[2] By careful hydrolysis of pectic acid; three isomeric tetragalacturonic acids have been isolated, differing in their optical properties, reducing power, etc. These acids have been shown to possess a cyclic structure, only tetragalacturonic acid B having a free aldehyde group. Ehrlich[12] has described a new pectic enzyme, pectolase, isolated from old cultures of *Perisporaceae* and shown to be present also in taka-diastase, diastase, and emulsin, which was able to hydrolyse these cyclic acids to (mono) galacturonic acid and was also able to liberate soluble pectic compounds from the insoluble protopectin. Ehrlich has suggested that the cyclic tetragalacturonic acids are normal intermediates in the enzymatic degradation of pectin.

Constitution of Long-chain Fatty Acids from Natural Sources.

F. Francis, S. H. Piper, and T. Malkin[13] have synthesised the *n*-fatty acids from C_{17} to C_{26}, and have made a study of the melting points and *X*-ray spacings of the acids, their ethyl esters, and of equimolecular mixtures of the acids. The melting points of the odd and the even acids lie on two smooth curves. Two important types of spacing are given by each acid, and when these are plotted against the number of carbon atoms four straight lines are obtained, two belonging to the even and two to the odd carbon acids. The authors call attention to the fact that reliance cannot be placed on melting point or " mixed " melting point for purposes of identification. For instance, acids of carbon content 20 and 21 atoms, and the following mixtures, 21 + 22, 22 + 23, 22 + 23 + 24, all melt between the limits 74·9° and 75·2°.. The *X*-ray spacings and melting points of mixtures of known composition convince the authors that a *n*-fatty acid cannot be considered pure unless it has the correct melting point and correct acid value and gives *both* *X*-ray spacings. They have analysed arachidic, lignoceric, cerotic, and montanic acids prepared from various natural sources, and the acids obtained by oxidation of the alcohols present in Chinese wax and carnauba wax. All were shown to be mixtures of *n*-fatty acids and there was no indication of the presence of so-called *iso*-acids. The authors show that by intense fractionation it is possible to obtain pure acids from natural sources. Samples of lignoceric acid prepared by Dr. Brigl from beechwood tar and of cerotic acid prepared by Professor Holde from Chinese wax were shown to be pure *n*-tetracosanoic acid and *n*-hexacosanoic acid respectively.

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[11] *Biochem. J.*, 1928, **22**, 381; *A.*, 1928, 559.

[12] *Cellulosechem.*, 1930, **11**, 140, 161; *A.*, 1163.

[13] *Proc. Roy. Soc.*, 1930, [*A*], **128**, 214; *A.*, 1161.

Glutathione.

Conclusive evidence has now been obtained that this tripeptide is γ-glutamylcysteinylglycine, $HO_2C{\cdot}CH(NH_2){\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}CH(CH_2{\cdot}SH){\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO_2H$, by E. C. Kendall, H. L. Mason, and B. F. McKenzie.[14] If glutathione is first oxidised to the corresponding sulphonic acid by means of bromine, and then treated with sodium hypobromite, it yields one molecule of carbon dioxide and a substance from which, before or after further treatment with nitrous acid, succinic acid and glycine are liberated by hydrolysis with hydrochloric acid. If glutathione is oxidised with hydrogen peroxide in the presence of ammonia, succinic acid is not liberated by the oxidation, but a significant percentage of the total glutamic acid can be separated as succinic acid after hydrolysis. Also, if glutathione is treated with nitrous acid and then with alkaline hypobromite, succinic acid cannot be isolated until after hydrolysis. Finally, if glutathione is oxidised with chloramine-T, the mononitrile of succinic acid is not liberated in significant amount, but succinic acid can be recovered after hydrolysis. These reactions show that glutathione must be either (1) glutamylglycylcysteine or (2) glutamylcysteinylglycine, the free amino-group of the glutamic acid being in the γ-position to the peptide linkage. Since the product of interaction of glutathione ethyl ester hydrochloride with magnesium phenyl bromide yields, on hydrolysis, diphenylacetaldehyde, it is probable that the carboxyl group of the glycine is free, and constitution (2) the correct one.

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[14] *J. Biol. Chem.*, 1930, **87**, 55; **88**, 409; *A.*, 945, 1299.

It will be recalled that (Sir) F. G. Hopkins [15] showed that when glutathione was boiled in aqueous solution much decomposition occurred, and together with unidentified products the diketopiperazine of glycine and cysteine (or, in the case of the disulphide form, diglycylcystine dianhydride) was isolated. Kendall and his co-workers find that, by heating glutathione in aqueous solution at 62° for 120 hours, hydrolysis to pyrrolidonecarboxylic acid and a dipeptide of glycine and cysteine occurs. On treatment of the latter with sodium hypobromite or with nitrous acid, followed by acid hydrolysis, glycerol was isolated, though in poor yield. The dipeptide was next oxidised to the disulphide, this condensed with 2 : 3 : 4-trinitrotoluene, and the product hydrolysed with hydrochloric acid. Glycine was again isolated, showing conclusively that the dipeptide was cysteinylglycine, and that glutathione must be γ-glutamylcysteinylglycine.

Additional evidence that glycine occupies a terminal position in the molecule has been furnished by B. H. Nicolet.[16] Glutathione was condensed directly with ammonium thiocyanate and acetic anhydride to give a compound $C_{16}H_{19}O_6N_5S_3$. This was condensed with benzaldehyde in the presence of acetic acid and sodium acetate to give a compound which, when hydrolysed with sodium hydroxide, gave a 50% yield of benzylidenethiohydantoin. The compound $C_{16}H_{19}O_6N_5S_3$ is therefore regarded as a bisthiohydantoin, in the formation of one of the thiohydantoin groups of which glycine must take part. It follows, then, that glycine occupies a terminal position in the molecule.

W. Grassmann, H. Dyckerhoff, and H. Eibeler [17] show that glutathione is not hydrolysed by pepsin, pancreatic proteinase, papain, or the dipeptidase and aminopolypeptidase from yeast and intestine. It is, however, readily attacked by pancreatic carboxypolypeptidase, which hydrolyses only one peptide linkage, yielding the total glycine in the free state and a peptide residue recovered in 90% yield. They consider that this shows the glycine to be at the end of the chain and that the carboxyl group is free.

This clarification of the chemical nature of glutathione has, unfortunately, introduced considerable uncertainty as to its actual physiological rôle in the pure condition. The earlier preparations possessed such characteristics as constituted glutathione a chemical catalyst in the interaction between atmospheric oxygen and fats, proteins, and the "insoluble, thermostable residue" left after exhaustive extraction of tissue.[18] All of these substances are oxidised in the presence of impure glutathione, which in turn is re-oxidised by oxygen gas. N. U. Meldrum and M. Dixon,[19] however, now indicate that glutathione when pure possesses these properties only in respect of the fats, where its catalytic activity is known to occur at an acidity not found in animal tissues. It appears that in all preparations of glutathione there exists in varying degree some hydrolytic product to which, in the presence of iron or copper ions, the autoxidisability of reduced glutathione must be attributed. Pure glutathione even in the presence of iron is not autoxidisable. Neither are other cysteine peptides. Nevertheless, the evidence presented by these authors indicates that the fission product is closely comparable in properties with cysteine itself. Thus, though existing evidence as to the function of the thiol group in conjunction with iron in a respiratory capacity is in no way affected, the actual participation of the tripeptide, glutathione, in this capacity has become much open to question.

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[15] *Ann. Reports*, 1929, **26**, 222.

[16] *J. Biol. Chem.*, 1930, **88**, 389; *A.*, 1299.

[17] *Z. physiol. Chem.*, 1930, **189**, 112; *A.*, 1067.

Recent attempts to show the presence of glutathione in plant tissues are not very convincing.[20]

Muscle Contraction.

The investigation of the physical and chemical processes which constitute the mechanisms of muscle contraction continues to absorb much of the energies of biochemists. In recent years considerable information concerning the chemical nature of the substances participating in the muscle process has accumulated, but the more purely physical side has been somewhat neglected.

In a highly interesting series of studies of the physical chemistry of muscle globulin, J. T. Edsall[21] directs attention to this neglect when he says: "Knowledge of the energy-liberating reactions in muscle has made enormous strides in the past 20 years, and far surpasses our knowledge of the machinery which they set in motion. It seems beyond doubt that the proteins play a large—if not the largest—part in this machinery. It is to be expected that the physico-chemical properties of the isolated protein will be found intimately related to its function within the muscle fibre." Edsall describes the preparation of muscle globulin, which is regarded as identical with the myosin of Danilewsky, von Fürth, and Weber, and with the paramyosinogen of Halliburton, although the term myosin is reserved, in a later paper of the series, for the anisotropic protein responsible for the double refraction of flow. Muscle globulin, if kept in the cold, protected from bacteria, dissolved in salt, at p_H 6·5 to 7·5 preserves its properties unchanged over a period of several months. The protein is insoluble in all salt concentrations between p_H 5 and 6, but it possesses an extraordinary affinity for water, from which it cannot be separated without some radical change in the protein itself. Even concentrated precipitates of the protein contain 98% of water, and it remains undenatured only in the presence of a large amount of water. This phenomenon may, as Edsall suggests, have a special physiological significance, since it has been recorded that no significant change occurs in the water content of skeletal muscle, even in cases of profound dehydration, when the fluid of the intercellular spaces is greatly depleted and the blood volume is diminished well below normal. When muscle weight is lost, proteins and salts are lost along with the water removed. In other words, the muscle appears to lose water to any extreme degree only when the protein is broken up and lost as well. The behaviour of muscle globulin suggests that the water is directly held by the protein, and that this water-holding power is not lost when the protein is extracted from the muscle.

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[18] *Ann. Reports*, 1925, **22**, 225. [19] *Biochem. J.*, 1930, **24**, 472; *A.*, 803.

[20] W. H. Camp, *Science*, 1929, **69**, 458; *A.*, 1929, 1499; V. B. White, *ibid.*, 1930, **71**, 74; *A.*, 826.

[21] *J. Biol. Chem.*, 1930, **89**, 289.

In two further communications A. L. von Muralt and J. T. Edsall[22] have published many interesting observations on the physical properties of muscle globulin. It is found that the protein shows double refraction of flow, which is ascribed primarily to the orientation of anisotropic particles and secondarily to photoelastic phenomena. Apparatus is described for measuring the angle of isocline (the angle at which the arms of the black cross appear when polarised light is passed through a solution of the protein in a rotating cylinder). The measurements of the angle of isocline are interpreted as indicating a monodisperse system, that is, the muscle globulin particles are of uniform shape and size. The angle of isocline of muscle globulin solutions is independent of age. After repeated washing of the muscle globulin solution, the preparation becomes practically salt-free and forms a clear gel even at an extremely low protein concentration (about 0·3%). Merely by vigorous shaking, this gel is transformed to the fluid state and sets again to a gel in a few minutes. It is therefore a thixotropic gel.[23]

The double refraction of flow shown by muscle globulin solutions is intimately related to the chemical nature of the protein solution.

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[22] *J. Biol. Chem.*, 1930, **89**, 315, 351.

[23] A. Szegvari and (Frl.) E. Schalek, *Kolloid-Z.*, 1923, **32**, 318; **33**, 326; *A.*, 1923, ii, 423; 1924, ii, 115.

Thus it is found that typical denaturing agents produce rapid and complete destruction of the double refraction of flow, which appears, therefore, to be a property only of the undenatured protein. From the work of H. Stuebel[24] it has been inferred that oriented rod-shaped particles, small compared with the wave-length of light, are present in the intact muscle and are responsible for its double refraction. The double refraction and other properties of myosin solutions indicate that they may contain these rod-shaped particles, and also point to the probable location of the myosin in the anisotropic disc of the cross-striated muscle fibre. It seems highly probable that these remarkably interesting investigations may elucidate new aspects of the functional activity of the muscle, and in any case they constitute a new and welcome attack, by established methods of physical science, on this very complex biological problem. Similar remarks may be made concerning the investigations of G. Boehm and K. F. Schotzky,[25] who have obtained *X*-ray diagrams of living muscle in a state of rest and of excitation.

Despite the wealth of new discoveries made in recent years concerning the chemical processes of muscle contraction, some recent observations of O. Meyerhof[26] suggest that there are still material gaps in our knowledge. Meyerhof has employed a thermo-electric method for measuring the depression of freezing point of muscle in fatigue and in rigor. In prolonged fatigue and rigor the observed depression is some 30% greater than would be expected on the basis of the known products of hydrolysis. Similar conclusions are reached by A. V. Hill and P. S. Kupalov,[27] who find that the increase of osmotic pressure in the fluids of a stimulated muscle is about 2·8 times as great as would be exerted by the lactate ions produced, if dissolved in the " free " water of the muscle. It is 1·8 times as great as would correspond to the lactate ions together with the creatine liberated by the breakdown of phosphagen, and is appreciably greater than can be accounted for by all the chemical changes at present known, or suspected, to occur in stimulated muscle. A. V. Hill[28] defines the " free " water fraction as the weight of water in 1 gram of fluid or tissue which can dissolve substances added to it with a normal depression of vapour pressure. The " free " water fraction of frog's muscle, whether resting or in rigor, is about 0·77, or perhaps a little greater, the total water fraction being 0·80 or 0·81. On the other hand, O. Meyerhof and F. Lipmann[29] find that the p_H change observed in a muscle during a prolonged series of twitches agrees well with that calculated from the lactic acid formed and the phosphagen split. The muscle at first becomes more alkaline and only in an advanced state of fatigue does it become more acid. The explanation of the phenomenon is found in the fact that the breakdown of creatinephosphoric acid, which in the first stages of fatigue is large compared with the simultaneous formation of lactic acid, increases the amount of basic equivalents.

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[24] *Arch. ges. Physiol.*, 1923, **201**, 629. [25] *Naturwiss.*, 1930, **18**, 282; *A.*, 637.

[26] *Biochem. Z.*, 1930, **226**, 1; *A.*, 1614.

[27] *Proc. Roy. Soc.*, 1930, [*B*], **106**, 445. [28] *Ibid.*, p. 477.

[29] *J. Physiol.*, 1930, **69**, Proc. XXI; *A.*, 1211; *Naturwiss.*, 1930, **18**, 330; *A.*, 810.

Muscle Contraction without Production of Lactic Acid.—In the field of muscle chemistry one of the most interesting and significant discoveries announced during the past year concerns the action of iodoacetic acid on the lactic acid formation of contracting muscle. Early in the year it was announced by E. Lundsgaard[30] that the post-mortem formation of lactic acid in the muscles of rabbits and frogs poisoned by sodium iodoacetate was completely inhibited. At the same time the contractile power of the muscle did not suffer damage. Muscles treated with sodium iodoacetate will contract with a hydrolytic cleavage of the phosphagen, which takes place even more rapidly than in normal muscle, and without lactic acid formation. After total breakdown of the phosphagen the muscle remains in a state of contraction. The phosphoric acid of the phosphagen is, under these conditions, rapidly and completely converted into hexosephosphoric acid. On the basis of these observations it was suggested that phosphagen might be the energy-producing substance in muscle activity, and that the production of lactic acid might cause progressive resynthesis of the hydrolysed phosphagen. Later, Lundsgaard showed that the anaerobic resynthesis of phosphagen was abolished after the muscle had been treated with iodoacetate, but on the other hand, in the presence of oxygen, the poisoned muscle did more work than under anaerobic conditions and showed a smaller diminution in phosphagen content. This result is ascribed to oxidative resynthesis of phosphagen. The chronaxie of the poisoned muscle is normal. O. Meyerhof, E. Lundsgaard, and H. Blaschko[31] have shown, by a comparison of the total anaerobic development of tension with the decomposition of phosphagen, that the whole of the energy for anaerobic contraction with the poisoned muscle is derived from phosphagen. Reference has already been made to the observations of Meyerhof and Lipmann on the change of p_H during muscle activity. As might be anticipated these observers[32] have demonstrated that in the presence of iodoacetic acid only the alkaline phase of the change is observed, and that when the muscle is arrested in contracture the alkalinity is maximal.

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[30] *Biochem. Z.*, 1930, **217**, 162; *A.*, 368.

[31] *Naturwiss.*, 1930, **18**, 787; *A.*, 1312.

[32] *Biochem. Z.*, 1930, **227**, 84.

Two further communications by Lundsgaard[33] extend these remarkably interesting observations. It is shown that iodoacetic acid completely inhibits alcoholic fermentation by living yeast and by zymase preparations, but in neither case is hexosephosphoric acid formation observed. The actions of invertase, ptyalin, and catalase are not affected by iodoacetic acid. In general, in the presence of iodoacetic acid, *oxidative* processes involving carbohydrates are able to proceed normally after *glycolysis* is completely inhibited.[34]

In addition to these observations concerning the energy sources of muscle contraction, a recent paper by G. Embden and E. Metz[35] directs attention to the fact that bromo- and iodo-acetic acids cause a marked diminution in the solubility of the muscle proteins, similar to that observed by H. J. Deuticke[36] in fatigued muscles. It would appear to be highly probable that the halogenated acetic acids are destined to be of great service in elucidating, and possibly even in revolutionising, the complex chemistry of the muscle processes.

It has been recognised for many years that fluorides inhibit fermentation and glycolysis, and F. Lipmann[37] has pointed out that, if muscles are poisoned with fluoride in such concentration as to leave unimpaired their contractile power, such contraction should occur without lactic acid formation. This he shows to be the case, the contraction occurring with decomposition of phosphagen, esterification of hexose with phosphoric acid, and hydrolysis of adenylpyrophosphoric acid. The mechanism of the action of iodoacetic acid and of fluoride on the lactic acid-forming ferment complex is similar, save that the former acts slowly and is irreversible, whereas the latter acts instantaneously and is reversible.

Phosphagen.—Continuing his observations already summarised and in support of his views[38] regarding the relation between phosphagen and rate of excitation, D. Nachmansohn[39] has shown that the increased extent of decomposition of phosphagen caused by veratrine is exactly proportional to the increased rate of excitation caused by the drug. On the other hand, curare and the ammonium bases generally produce a marked reduction in the extent of decomposition, the greatest effect in this respect being observed with trimethyloctylammonium iodide. This base has been used by

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[33] *Biochem. Z.*, 1930, **220**, 1, 8; *A.*, 958, 954.

[34] *Ibid.*, 1930, **227**, 51.

[35] *Z. physiol. Chem.*, 1930, **192**, 233.

[36] *Pflüger's Arch.*, 1930, **224**, 1.

[37] *Biochem. Z.*, 1930, **227**, 110.

[38] *Ann. Reports*, 1929, **26**, 232.

[39] *Biochem. Z.*, 1929, **213**, 262; *A.*, 1929, 1484.

O. Meyerhof and D. Nachmansohn[40] in investigating the synthesis of phosphagen in living muscle. It is found that the anaerobic resynthesis of phosphagen in living muscle after decomposition during tetanus is as great, expressed absolutely, in muscle poisoned with trimethyloctylammonium iodide as in the unpoisoned muscle, but is much greater when expressed as a percentage of the total decomposition. Aerobic resynthesis of phosphagen is observed to occur both after previous decomposition on admission of oxygen, and without previous decomposition when the muscle is placed in Ringer's solution saturated with oxygen, especially after addition of phosphate. The aerobic resynthesis after previous decomposition proceeds more quickly and completely at lower temperatures and most quickly at $-0{\cdot}5°$ to $-1°$. The molecular ratios, phosphate synthesised : oxygen used, and phosphate synthesised : lactic acid disappearing, both give values of 5.

B. Kisch[41] has published some interesting observations on the occurrence of phosphagen in the electric organ of *Torpedo*. The amount present is found to be about the same as that of the general musculature. In the fresh unstimulated organ 77% of the phosphorus of the acid extract is present as phosphagen. During activity of the organ and during asphyxiation the amount of phosphagen rapidly diminishes, but resynthesis occurs during rest in the presence of oxygen. Thus the analogies between the electric organ and the skeletal muscles developed on morphological grounds are supported by these biochemical observations.

The Adenylic Acid Complex of Muscle.—There is now a general acceptance of the view that the adenine present in an aqueous extract of muscle occurs as a nucleotide. The observations of K. Pohle,[42] A. Dmochowski,[43] and P. Ostern[44] are in accord in this respect, and the further association of the nucleotide (adenylic acid) with pyrophosphoric acid, an association first indicated by K. Lohmann,[45] is supported by the data of C. H. Fiske and Y. Subbarow.[46] The last-mentioned observers do not regard adenylic acid as such, as a normal constituent of muscle, but find it to be a decomposition product of a substance which is precipitated as the calcium salt from a protein-free muscle filtrate. This substance yields adenine, carbohydrate, and three molecules of phosphoric acid, two of which are readily removed by acid hydrolysis.

Concerning the significance of adenylic acid as the source of muscle ammonia, G. Embden and G. Schmidt[47] have published some convincing data. The enzymes of fresh frog-muscle were destroyed by acid treatment and the muscle was exposed to the action of an enzyme capable of deaminising muscle adenylic acid only.[48] The ammonia eliminated by this procedure corresponds with that obtained by exposing the minced muscle for 3 to 4 hours in a slightly alkaline solution. It is concluded, therefore, that the ammonia formed in a short autolysis of frog's muscle is derived exclusively from the muscle adenylic acid, and that it is now possible to exclude even adenosine as a possible source. Adenylic acid may participate in reactions involving more profound degradation of its molecule than this deamination. In some of the results published by G. Embden, J. Hefter, and M. Lehnartz[49] there is a suggestion that at the moment of contraction a fission of adenylic acid, or of its deamination product, inosinic acid, may occur with the formation of orthophosphoric acid, and K. Pohle[50] has suggested adenylic acid as a possible precursor of endogenous uric acid.

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[40] *Biochem. Z.*, 1930, **222**, 1; *A.*, 1210. [41] *Ibid.*, 1930, **225**, 183; *A.*, 1464.
[42] *Z. physiol. Chem.*, 1929, **185**, 9; *A.*, 1929, 1479.
[43] *Biochem. J.*, 1929, **23**, 1346; *A.*, 1930, 238.
[44] *Biochem. Z.*, 1930, **221**, 64; *A.*, 945. [45] *Ann. Reports*, 1929, **26**, 231.
[46] *Science*, 1929, **70**, 381; *A.*, 1930, 492.

Adenylic Acid and the Kidney.—Considerable interest attaches to the occurrence and functions of adenylic acid in kidney tissue. G. Embden and H. J. Deuticke[51] have isolated the acid from this source and shown it to be identical with that obtained from muscle. It is acted upon by the specific deaminase of rabbit's muscle. B. E. Holmes and A. Patey[52] have studied the ammonia-forming systems which occur in washed kidney tissue. One of these acts aerobically and has an optimum of p_H 5·2 or lower. A second aerobic system, acting upon glycine, and an anaerobic system are also shown to be present in the kidney.[53] It is suggested that the first-mentioned system is concerned in the normal production of ammonia by the kidney, as this is known to be greatest when the urine is acid. It is not yet possible to state whether or not adenylic acid is the ammonia-precursor in this system. There is, however, general agreement that adenylic acid can be completely deaminated under anaerobic conditions. Therefore, although it may be the source of some of the ammonia in the urine, it cannot be the substrate of the particular aerobic system studied, and the p_H optimum curves do not suggest that it is the substrate for extra ammonia formation in the case of an acid urine.

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[47] *Z. physiol. Chem.*, 1930, **186**, 205; *A.*, 494.

[48] *Ann. Reports*, 1929, **26**, 228.

[49] *Z. physiol. Chem.*, 1930, **187**, 53; *A.*, 637.

[50] *Loc. cit.*

[51] *Z. physiol. Chem.*, 1930, **190**, 62; *A.*, 1203.

[52] *Biochem. J.*, 1930, **24**, 1564; *A.*, 1614.

[53] A. Patey and B. E. Holmes, *ibid.*, 1929, **23**, 760; *A.*, 1929, 1194.

Enzymic Hydrolysis of Glycogen.

A. D. Barbour [54] records the hydrolysis of glycogen by means of a glycerol extract of fresh muscle or liver tissue. The hydrolysis is carried out for 5 hours at the optimum p_H of 6·3. The sole product of the action of the muscle extract upon the glycogen is a trisaccharide, $C_{18}H_{32}O_{16}$, having $[\alpha]_{5461} + 181°$, and 30% of the reducing power of glucose. It is readily converted into the anhydro-trisaccharide, $C_{18}H_{30}O_{15}$, having $[\alpha]_{5461} + 187°$, and 8·5% of the reducing power of glucose. The digestion of glycogen by salivary or pancreatic amylase appears to follow a course different from that of the muscle and liver enzymes. Attempts to use the enzyme for the synthesis of glycogen from the trisaccharide and its anhydro-derivative were not successful. If the trisaccharide can be obtained in reasonable amount, it would become a matter of great interest and importance to subject it to the recognised methods of structural investigation in the sugar group, more especially in view of the apparent chemical identity of trimethyl glycogen and trimethyl starch.[55] It is of interest to recall here the preparation from glycogen by H. Pringsheim and G. Will [56] of a trisaccharide derivative which they called glycogesan. It was obtained by chemical means. Under the influence of pancreatic amylase, glycogesan was degraded to maltose, fission being practically quantitative if yeast complement was added. Although glycogesan behaved as a trisaccharide on cryoscopic investigation, the facts that it formed a colloidal solution in boiling water and possessed the same optical activity and iodine colour reaction as glycogen suggest that it has a greater molecular complexity than the trisaccharide described by Barbour.

Alcoholic Fermentation.

In an important paper by R. Robison and W. T. J. Morgan [57] on the phosphoric esters of alcoholic fermentation a detailed description is given of the methods of fermentation and separation employed. The details will be of great service to other workers in this field. The distribution of the total esterified phosphorus amongst the four known esters is given for a number of fermentation experiments with yeast-juice, zymin, and dried yeast. There is appended a table, taken from this paper, which records analytical data of the barium salts of these esters :

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[54] *J. Biol. Chem.*, 1929, **85**, 29; *A.*, 1930, 249.

[55] W. N. Haworth, E. L. Hirst, and J. I. Webb, *J.*, 1929, 2479; *A.*, 1930, 72.

[56] *Ber.*, 1928, **61**, [*B*], 2011; *A.*, 1928, 1225.

[57] *Biochem. J.*, 1930, **24**, 119; *A.*, 374.

Ester.	P, %.	Reducing power as glucose. H. and J., %.	Reducing power as glucose. Iodine, %.	Seliwanoff fructose, %.	$[\alpha]_{5461}$.
Barium fructosediphosphate	10·16	12	2	10	+ 3·5°
,, glucosemonophosphate	7·85	36	41	0	+19·5
,, fructosemonophosphate (Neuberg)...	7·85	36	2	22	+ 0·7
,, trehalosemonophosphate	5·57	0	0	0	+132

In the course of this work some indication has been obtained of the existence of a fifth ester, forming, at most, only a very small proportion of the fermentation products. Following on the discovery of pyrophosphate as a constituent of muscle,[58] E. Boyland [59] has shown that it also occurs in living yeast and forms about one-fourth of the total phosphorus. Pyrophosphate added to fermenting zymin is rapidly hydrolysed to orthophosphate, which then reacts in the usual way. Evidence is obtained of the presence in yeast of a pyrophosphatase which is distinct from hexosephosphatase. The distribution of phosphorus compounds in fresh English brewer's yeast (as mg. of phosphorus per g. of yeast) is given as follows :

Total phosphorus	3·25	Hexosediphosphate	0·38
Orthophosphate	1·37	Hexosemonophosphate	0·72
Pyrophosphate	0·68	Nucleic acid	0·07
Organic phosphorus	1·17		

A. Harden and M. G. Macfarlane [60] have made experiments in which mixtures of sand and yeast were ground for different periods and the resultant total mass, without pressing out, was tested for the rate of fermentation and response to phosphate. At least 80% of the diminution in the rate of fermentation which occurs is ascribed to the process of grinding, during which the yeast acquires the power of responding to phosphate. The conclusion is drawn that the grinding process mainly affects the mechanism of hexosephosphatase action. M. G. Macfarlane [61] has published a study of the action of disodium arsenate on hexosephosphatase in which it is shown that the accelerating action takes place only in the presence of yeast extract and cannot be obtained without an accompanying fermentation. Although this observation does not elucidate the mechanism of the accelerating action of arsenate, it does dispose of earlier theories which ascribed it to a direct effect upon the hydrolysis. In relation to this question it is significant that K. Lohmann[62] has found that the hydrolysis of Robison's monophosphoric acid ester in frog-muscle pulp is accelerated by arsenate only after the mono-ester has been further esterified to form the Harden and Young di-ester.

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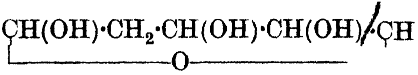
[58] *Ann. Reports*, 1929, **26**, 230.
[59] *Biochem. J.*, 1930, **24**, 350; *A.*, 817.
[60] *Ibid.*, p. 343; *A.*, 818.
[61] *Ibid.*, p. 1051; *A.*, 1317.

The Sugar of Animal Nucleic Acid.

During the past year the long-debated problem of the nature of the sugar component of animal nucleic acid would at least appear to have been settled. The fission of animal nucleic acid into its component nucleotides presents much more difficulty than is encountered in the case of the plant acid. But despite these difficulties P. A. Levene and E. S. London[63] have succeeded in effecting this disruption and in isolating guanine nucleoside together with smaller quantities of hypoxanthine, thymine, and cytosine nucleosides. Using combined gastric and intestinal fistulæ, they subjected solutions of animal nucleic acid to the action of the intestinal juices of the dog *in vivo* and subsequently for longer periods *in vitro*, or alternatively the juices were collected from the fistulæ and added to solutions of nucleic acid. Levene and London[6
prepared from guanine nucleoside a sugar having the compositi
of a deoxypentose, $C_5H_{10}O_4$, to which, pending its identificat
they gave the name thyminose. It gave with Kiliani's reager
specific colour reaction for this type of sugar, and a Wills
Schudel iodometric oxidation proved it to be an aldose. I
lævulic acid on being treated with sulphuric acid and v
fore a straight-chain pentose. The later work of P. A. 7
T. Mori,[65] and of P. A. Levene, L. A. Mikesk.., and T
to the identification of thyminose as *d*-2-deoxyribose



$$\underbrace{\mathrm{CH(OH)\cdot CH_2\cdot CH(OH)\cdot CH(OH)\cdot CH}}_{\mathrm{O}}$$

The new sugar is therefore a reduction pro
plant nucleic acid. It affords, so far as
the first instance of the occurrence of a
product.

The Sugar of Pentosuria.—The poss
sugar of animal nucleic acid to the
the present remain speculative. In

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[62] *Biochem. Z.*, 1930, **222**, 324; *A.*, 1?

[63] *J. Biol. Chem.*, 1929, **81**, 711; *A.*,

[64] *Ibid.*, 1929, **83**, 793; *A.*, 1929, 13

[65] *Ibid.*, p. 803; *A.*, 1929, 1277.

variously identified as *dl*-arabinose, *l*-arabinose, *dl*-ribose, *l*-ribose, *d*-xyloketose, or simply as a *d*- or an *l*-rotatory pentose. In view of these curious variations, but more especially in view of the great interest of Levene's new results, a re-examination of all the available data seems desirable. During the past year two studies of the sugar of pentosuria have appeared. I. Greenwald,[67] on the basis of four cases, identifies the sugar as *d*-xyloketose, and P. Hári,[68] with five cases at his disposal, finds that the sugar belongs to the xylose group but does not record very convincing evidence regarding its optical rotation. It is perhaps worthy of note that H. O. Calvery [69] has isolated adenosine (adenine-*d*-riboside) from normal human urine. No trace of the phosphorylated compound (adenylic acid) was detected. The adenosine was isolated from a mixed urine and the yield was small, so the nucleoside might easily have had its origin in the urine of a few individuals, and therefore may not be of common occurrence. Its presence in urine may bear some relationship to the uric acid–pentose compound first reported in urine by A. R. Davies, E. B. Newton, and S. R. Benedict.[70]

The Sugars of the Tubercle Bacillus.

In the Reports for 1926 [71] and 1929 [72] attention was directed to
important rôle of carbohydrates in immunological reactions.
work there summarised dealt mainly with the sugars of the
ococcus group of organisms. In the past year much inform-
as accumulated concerning the similarly specific sugars of
rcle bacillus. From tubercle bacilli propagated in a
sugar-free medium and also from tuberculin, M. Maxim [73]
a polysaccharide which on hydrolysis yields *d*-mannose
ose. The same two carbohydrates are reported by
[74] to be present in the polysaccharide isolated from
media in which tubercle bacilli had grown. P.
Alpine [75] likewise confirm this and in addition
gar acid. E. Chargaff and R. J. Anderson [76]
annose and arabinose together with galactose
ccharide extracted by toluene along with
illi. R. J. Anderson and E. G. Roberts [77]

A., 1311.

A., 1469.

A., 633.

[70] *Ibid.*, 1922, **54**, 595.

[72] *Ibid.*, 1929, **26**, 239.

., 1219.

A., 678.

[77] *J. Biol. Chem.*, 1930, **89**, 611.

find glucose, mannose, and inositol in the sugar fraction of the tubercle phosphatide described in the Report of last year. The occurrence of *d*-arabinose in these sources is of interest, since *l*-arabinose is the usual variety found in nature. A useful review of the present state of these investigations will be found in the article by T. B. Johnson and A. G. Renfrew.[78] The polysaccharide examined by Renfrew gave precipitin reactions at a dilution of 1 in 1,500,000, from which it may be inferred that the tubercle polysaccharide is functionally similar to those of the pneumococci.

A study of the molecular size of the specific polysaccharide of Type III pneumococcus has been made by F. R. Babers and W. F. Goebel,[79] using the diffusion method of Northrop and Anson.[80] The result gives a molecular weight of 118,000. Incidentally the same method has been applied by P. A. Levene and A. Rothen [81] to the polysaccharide of ovomucoid, which appears to consist exclusively of glucosamine and mannose. The result in this case indicates a molecular weight of 2000 and it is inferred that the polysaccharide consists of four trisaccharide units each containing 1 molecule of glucosamine and 2 molecules of mannose.

The Reducing Substances of Blood.

In view of the widespread use of various techniques for determining the reducing substances of blood (usually referred to a
"blood sugar") a paper published by J. M. Gulland and R.
Peters [82] will be of interest. In this a study is recorded of
reducing substances of pigeon's blood. It has frequently
observed that the total reducing value of avian blood deter
by the usual methods is considerably higher than that of ma
blood. For instance, for normal hen's blood the Hage
Jensen method has given values as high as 0·253%, wh
appear to place normal avian blood within the rang
diabetic values. Gulland and Peters find in pigeon's
same method) an average of 0·200%, of which only 0·
can be regarded as glucose or similar reducing
filtrates prepared by different methods contain diff
of ergothioneine, uric acid, and glutathione,
sulphhydryl compounds. Zinc filtrates made b
Jensen method, which do not contain aliph
pounds (an observation confirmed by M.

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[78] *Amer. Rev. Tuberculosis,* 1930, **22**, 655.

[79] *J. Biol. Chem.*, 1930, **89**, 387. [80]

[81] *J. Biol. Chem.*, 1929, **84**, 63; *A.*, 1929

[82] *Biochem., J.* 1930, **24**, 91; *A.*, 360.

[83] *J. Biol. Chem.*, 1930, **87**, 761; *A.*,

most trustworthy for determining the reducing substances of avian blood, but these filtrates contain in addition to glucose, ergothioneine and some other unknown substances which reduce the ferricyanide reagent. Some 60% of the residual (non-glucose) reducing value is not accounted for by ergothioneine.

To judge from the number of papers published on the subject, the problem encountered by Gulland and Peters, perhaps in a less acute form, must be kept in mind in relation to the determination of the reducing substances of mammalian blood. That glucose is present as such in blood has been demonstrated by L. B. Winter,[84] who has been able to isolate the normal crystalline form of the hexose from blood filtrates. But it cannot be doubted that in the various methods used for determining blood sugar, other reducing substances in varying amounts are included from time to time in the glucose figure. A useful critical study of this question in which the Shaffer–Hartmann alkaline copper reagent is used, together with a consideration of the effects of different deproteinising agents upon the determination of blood sugar, has been published by S. L. Tompsett.[85] The reducing power of glutathione in relation to this problem is dealt with by M. R. Everett,[86] and the effect of acid hydrolysis on the total carbohydrate content of the blood is examined by F. Silberstein, F. Rappaport, and M. Wachstein.[87] Papers by J. Roche,[88] E. J. Bigwood and A. Wuil-ot,[89] and G. Fontès and L. Thivolle[90] should also be consulted.

The Coagulation of Hæmoglobin and its Reversal.

L. Anson and A. E. Mirsky[91] have brought to light a very
ing property of hæmoglobin which it probably possesses in
with other proteins. It has been the accepted view that
otein is coagulated or denatured the change which it has
s an irreversible one. Protein coagulation proceeds in
steps. The first, known as denaturation, is a change
rotein brought about by heat, the action of acid,
agents, which makes the previously soluble protein
isoelectric point. The second step is the pre-
soluble denatured protein. The latter, although
electric point, is soluble in acid or alkali. If,
denatured in a nearly isoelectric solution, a

851; *A.*, 1306.

A., 1306. [86] *Loc. cit.*

355; *A.*, 1929, 1477.

0, **12**, 636; *A.*, 1054.

930, 237. [90] *Ibid.*, p. 1212; *A.*, 237.

1, 133; 1930, **13**, 469, 477; *A.*, 102, 630.

visible precipitate results. But if a protein is denatured in acid or alkaline solution, no visible change results until the solution is made isoelectric; the protein is then precipitated. The second step in coagulation, the flocculation of the insoluble protein, is, as has long been known, reversible, since the flocculated protein may readily be redissolved. The first step in coagulation, denaturation, has hitherto not been reversed. When a solution of the coagulum in acid or alkali is brought to the isoelectric point, the protein is again precipitated; it is still denatured. Denaturation, therefore, is the important process in the investigation of the reversibility of coagulation.

Anson and Mirsky have been able to show in the first place that hæmoglobin, like all typical coagulable proteins, may be completely denatured, the test of complete denaturation being insolubility at the isoelectric point. Denaturation of the native hæmoglobin has been effected in a number of different ways, by heat in the presence of acid, by acid, by urea, and by shaking, and in all cases the results are the same. From preparations of completely denatured horse hæmoglobin Anson and Mirsky have prepared native carbon monoxide-hæmoglobin which is identical with the same pigment obtained directly from native hæmoglobin. "Reversed" hæmoglobin can be coagulated by heating, and in regard to its colour, absorption bands, gas affinities and other properties it is indistinguishable from native hæmoglobin which has not been through the denaturation process. By means of
crystallographic, spectroscopic, and gas-affinity measurements t
soluble native hæmoglobin prepared from coagulated horse hæ
globin cannot be distinguished from native hæmoglobin in ge
or from horse hæmoglobin in particular. Denatured hæmog
of various species cannot be distinguished from one anot
spectroscopic and gas-affinity measurements, but, on t
hand, after reversal of the coagulation the species' char
once more become observable. Anson and Mirsky h
yields of 75 and 80% of the reversed protein, which w
remove all possibility of their results being due to th
residue of native hæmoglobin attached to the m
natured protein. It is concluded that protei
general is probably reversible. In support of th
that, by the use of acid acetone, hæmoglobin m
ated into a precipitate of denatured globin an
of hæmatin. By gradual neutralisation the
be largely converted into a soluble native f
with hæmatin to form hæmoglobin.

It seems not improbable that the p

and its reversal may have a wide significance in the chemistry of the proteins as a whole. In the living cell the reversible coagulation of proteins at intersurfaces may play some part in determining the properties of semipermeable membranes, or in the mechanisms of muscle contraction.

Hæmocyanin.

During the period under review a considerable revival of interest in hæmocyanin has occurred and a number of interesting references to the pigment have appeared. None of the newer investigations supports the view that hæmocyanin is constituted on lines similar to hæmoglobin, that is to say, there is no evidence of the presence of a copper-porphyrin in its molecule. J. Roche [92] has shown that it is possible to separate the copper from hæmocyanin by adjusting the solution to p_H 2·5, by the addition of dilute hydrochloric acid, followed by dialysis. Such treatment applied to hæmoglobin transforms it into hæmatin and globin. No similar transformation is observed in the case of hæmocyanin. Degraded hæmocyanin, as Roche calls the copper-free substance, shows the same isoelectric point, buffering power, and solubility as natural hæmocyanin. It is concluded that no prosthetic group is liberated by this treatment, and that the presence of such in the hæmocyanin molecule is problematical. It is thought that the view taken by M. Henze [93] in 1901, namely, that hæmocyanin is a copper proteinate, is much nearer the truth than some of the views advanced nce that date. Roche has also shown an interesting difference ween the hæmocyanins of *Octopus* and *Limulus*. The pigment e former has an isoelectric point (p_H 4·8) close to that of the crust- pigments examined by E. Stedman and (Mrs.) E. Stedman,[94] the isoelectric point of *Limulus* hæmocyanin is much p_H 6·2—6·4), a fact which is possibly related to the much aic morphological characters of the king crab.

ons essentially similar to those of Roche have been J. B. Conant and W. G. Humphrey [95] and by A. he former investigators find the pigment to be a ination with a complex salt of an unknown amino- sulphur, which forms highly coloured complexes in this respect functions in a manner similar to of hæmoglobin. Schmitz suggests that the a protein combined with a complex copper

930, **7**, 207. [93] *Z. physiol. Chem.*, 1901, **33**, 370.

33; *A.*, 1927, 689.

30, **16**, 543; *A.*, 1304.

A., 1304.

compound which is of a peptide nature. It should be mentioned that the methods used by Conant and Humphrey and by Schmitz in degrading hæmocyanin were much more drastic than that employed by Roche. It is doubtful in view of Roche's results whether one can accept their evidence for the existence of a copper-containing prosthetic group of a peptide nature.

F. Hernler and E. Philippi [97] give the following composition of air-dried crystalline oxyhæmocyanin from *Helix pomatia* : C, 48·59; H, 7·04; N, 14·26; S, 0·71; Cu, 0·232. E. Philippi and F. Hernler [98] have published a further paper on the action of papain on their purified hæmocyanin, which confirms the earlier results of C. Dhéré and C. Baumeler [99] regarding the rapid formation of crystalline oxyhæmocyanin in the presence of papain and sodium fluoride. The ease of crystallisation is remarkable in view of the enormous molecular weight of 4,930,000 assigned by T. Svedberg [1] to hæmocyanin.

Female Sexual (Œstrous-producing) Hormone.

During the past two years activity in this field has greatly increased and in view of the fact that several workers have isolated crystalline products with considerable biological activities a review of the present position seems desirable.

The presence of an œstrous-producing hormone in the urine of pregnant women was first shown in 1927 by Aschheim and Zondek. Since that date many workers have entered the field and during the past year several claims have been made to have isolated the hormone in a crystalline form. H. Wieland, W. Straub, and T. Dorfmüller [2] described the preparation of an active crystalline material which melted at about 175° and finally became liqui
with decomposition at 210°, but no claim was made that the su
stance was pure. A. Butenandt [3] prepared an active crystal
substance which, from the constancy of its activity after recryst
ation and resublimation, he believed to be the hormone
The substance melted at 240°, with decomposition, an
analyses the formula $C_{23}H_{28}O_3$ or $C_{24}H_{32}O_3$ was ascribed t
was unsaturated and on account of its behaviour with
alkali it was suggested that the substance was a hydro
A. Butenandt and E. von Ziegner [4] later raised the melt
243—245°, and Butenandt [5] modified his first suggeste

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[97] *Z. physiol. Chem.*, 1930, **191**, 23; *A.*, 1461. [98]

[99] *Compt. rend. Soc. Biol.*, 1929, **101**, 1071. [1] *Ann. Rep*

[2] *Z. physiol. Chem.*, 1929, **186**, 97; *A.*, 1930, 255.

[3] *Naturwiss.*, 1929, **17**, 879; *A.*, 1930, 118.

[4] *Z. physiol. Chem.*, 1930, **188**, 1; *A.*, 646.

[5] *Ber.*, 1930, **63**, [*B*], 659; *A.*, 633.

$C_{21}H_{36}O_2$ and ascribed to the compound a structure closely analogous to that of the bile acids and sterols. Finally Butenandt[6] described new methods of preparing the hormone and assigned to it the formula $C_{18}H_{22}O_2$, with $[\alpha]_D + 156°$ and a melting point of 250—251°. It contains a hydroxyl group, a keto-group, and three double linkings. E. Dingemanse, S. E. de Jongh, S. Kober, and E. Laqueur[7] described a substance which appeared to be similar to that of Butenandt to judge from the melting point and analytical figures. E. A. Doisy, C. D. Veler, and S. Thayer[8] have also prepared what they claim to be the crystalline hormone, since their material possessed a constant activity and melting point after twenty recrystallisations from several different solvents. These workers later ascribed to their substance the formula $C_{18}H_{21}(OH)_2$ [*sic*], although their figures would agree equally well with formulæ having one less or one more hydrogen atom. The melting point was 243°. One double bond is stated to be present and the substance is weakly acidic.

In 1929, previous to the publication of the results described in the foregoing paragraph, G. F. Marrian[9] described the isolation from the urine of pregnancy of a crystalline œstrous-producing hormone to which he at that time, and as a result of preliminary investigations, ascribed the formula $C_{19}H_{30}(OH)_2$ or $C_{20}H_{32}(OH)_2$ and a melting point of 233—235°. Improved methods of isolation and purification of the hormone[10] eventually yielded a substance with a melting point of 281° having the constitution $C_{18}H_{24}O_3$. It has $[\alpha]_{5461} + 38°$. The substance has three hydroxyl groups, one of which is acidic and therefore presumably phenolic in character, nd indeed definite reactions for a phenolic group have been obtained. s activity is unchanged after numerous recrystallisations.

t will be observed that the formula most recently adopted by nandt differs from Marrian's formula only by H_2O, and Buten- himself suggests that Marrian's substance may be the hydrate hormone. The much higher optical rotation of Butenandt's l would tend to support this view, as would also the facts y one hydroxyl group is present whilst the remaining present in a ketonic or similar grouping. In any case 's conclusions seem now to be much closer to those of n they were some months ago. In a private com- arrian informs the Reporter that Butenandt has

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ysiol. Chem., 1930, **191**, 127, 140; *A.*, 1480.

ed. Woch., 1930, **56**, 301; *A.*, 1320.

Chem., 1930, **86**, 499; **87**, 357; *A.*, 821, 1069.

J., 1929, **23**, 1090; *A.*, 1929, 1495.

33; 1930, **24**, 435, 1021; *A.*, 254, 821, 1320.

recently isolated, in addition to the active substance $C_{18}H_{22}O_2$, the substance $C_{18}H_{24}O_3$ (Marrian's crystalline substance), and that he finds the latter to be physiologically active. It would therefore appear that both these substances are present in the urine of pregnancy, and that at some stage two hydroxyl groups are inserted in, or lost from, the hormone as it comes from the ovary without materially affecting the physiological activity.

It seems to the Reporter highly probable that all these workers are handling the same or very similar crystalline materials in varying degrees of purity. Owing to variations in the methods of biological assay employed by the various workers it is not possible to make the assay figures a satisfactory basis of comparison between different preparations. But it may be mentioned that Marrian's purest material has an activity of 8×10^6 mouse units per gram. On conversion into the acetate the activity fell to $3{\cdot}74 \times 10^6$ mouse units per gram. On the basis of the amount of the original substance present in the acetate, this activity corresponds to $5{\cdot}37 \times 10^6$ mouse units per gram. Thus the conversion of the substance into its acetate appeared to have decreased its physiological activity to a significant extent. The material regenerated from the acetate possessed an activity of $7{\cdot}4 \times 10^6$ mouse units per gram, from which it seems certain that hydrolysis of the acetate yielded the original substance again.

The Liver Constituent Curative of Pernicious Anæmia.

In the Report of two years ago attention was directed to the work of Cohn [11] and his collaborators on the concentration of the substance present in liver, which had a specific curative action in cases of pernicious anæmia. The opinion was then expressed that the properties of the substance suggested those of a salt of a fairl
complex organic acid. R. West and M. Howe [12] have now describ
the isolation of a crystalline derivative of an acid present in li
and active in pernicious anæmia. They give details of the pre
ation of an active amorphous material from a concentrated aq
solution of commercial liver extract. This material is st
acid to litmus and to methyl-red and contains approximatel
of carbon, 6·9% of hydrogen, and 10·6% of nitrogen. Fre
nitrogen is absent, but after acid hydrolysis one-half of th
is obtained in that form. A finely crystalline quinine
acid was obtained by gently warming its solution
quinine gradually until the reaction was neutral or sli
to litmus. Recrystallisation was easy and to this
assigned the provisional constitution $C_{20}H_{24}O_2$

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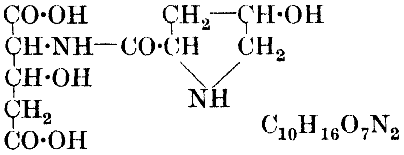
[11] *Ann. Reports*, 1928, **25**, 263. [12] *J. Biol. Chem*

Physiological tests on the substance after removal of the quinine showed it to be highly active in producing a reticulocyte response in cases of pernicious anæmia. When the quinine salt was decomposed with soda, and the quinine removed, a solution was obtained which after hydrolysis contained amino-nitrogen and gave the qualitative reactions of β-hydroxyglutamic acid. This acid was also isolated as its silver salt. Later, H. D. Dakin, R. West, and M. Howe [13] identified *l*-γ-hydroxyproline as a constituent of the original active substance. The latter is therefore regarded as the dipeptide of this acid with β-hydroxyglutamic acid. From the description of its properties given in these communications it would appear to have the constitution :



$C_{10}H_{16}O_7N_2$

l-*Thyroxine as a Constituent of the Thyroid Protein.*

C. R. Harington and W. T. Salter [14] have recorded the successful isolation of thyroxine from the thyroid gland by means of the action of enzymes alone. An alkaline sodium chloride extract of the gland was digested by successive additions of trypsin at p_H 8·5, and after precipitation at p_H 5, it was extracted with acid acetone and reprecipitated with ether. This precipitate was subjected to further tryptic digestion, and then precipitated at p_H 5 and redissolved in water with the aid of the least possible amount of ammonia. Pigmented impurities were removed by boiling with barium hydr-
xide. After precipitation at p_H 5 and solution in alkaline 80%
cohol, further impurities were precipitated with acid acetone.
e digestion product at this stage was not further acted upon by
nal erepsin or yeast peptidase. The product was dissolved in
ine, precipitated by dilution with water, dissolved in potassium
ate solution, decomposed with acetic acid, and reprecipitated
monosodium salt of thyroxine on cooling after boiling with
arbonate. The sodium salt on decomposition with acetic
led *l*-thyroxine. Comparative physiological tests on the
roduct and on pure *l*-thyroxine have shown that there
n to presume the existence in the thyroid gland of an
ole other than thyroxine, or of its existence there in an
form. Thus the isolation of thyroxine through the

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[13] *Proc. Soc. Exp. Biol. Med.*, 1930, **28**, 2.

[14] *Biochem. J.*, 1930, **24**, 456; *A.*, 820.

unaided action of a proteolytic enzyme supplies the final proof that the compound is present in the gland in peptide combination as a constituent of thyreoglobulin. Moreover the optical rotation of *l*-thyroxine isolated by the enzymic procedure proves the completeness of the resolution of *dl*-thyroxine already described by Harington.[15]

Acetylcholine from an Animal Source.

A matter of great physiological interest is the isolation of acetylcholine from the spleen of the ox and the horse by H. H. Dale and H. W. Dudley.[16] This is the first record of the natural occurrence of this substance in the animal body, although it has been widely employed in physiological experimentation. It was prepared artificially by Baeyer in 1867 and there are two later records of its isolation from plant sources. Its physiological interest lies in the correlation of its action with that of the parasympathetic nervous system just as adrenaline simulates the action of the sympathetic division of the autonomic nervous system. Dale and Dudley, after discussing these physiological problems, say : " But there has been a natural and proper reluctance to assume, in default of chemical evidence, that the chemical agent concerned in these effects, or in the humoral transmission of vagus [17] action, was a substance known, hitherto, only as a synthetic curiosity, or as an occasional constituent of certain plant extracts. Many things could be explained if the liberation of acetylcholine could be postulated; but the minuteness of the quantities required to produce the effects in question, and the extreme instability of the substance, while enhancing its theoretical fitness for the suggested functions, precluded any hope of its chemical identification at the sites of its possible liberation. . . . Its definite isolation from one organ has so far altered the position that, when an extract from, or a fluid in contact with the cells of, an animal organ can be shown to contain a principle having the actions, and the peculiar instability, of acetylcholine, it will be reasonable in future to assume the identification." H. W. Dudley [18] has published a separate description of the methods used in the difficult problem of separating acetylcholine from choline by means of their chloroplatinates. A further study by H. H. Dale and J. H. Gaddum [19] deals with the behaviour of denervated voluntary muscles in relation to the actions of the parasympathetic system and of acetylcholine. In this important paper much evidence is brought forward in support of the view that the vaso-dilator effects of parasympathetic nerves, and of sensory fibres stimulated antidromically, and the contractures of denervated muscles accompanying these actions, are due to the peripheral liberation of acetylcholine.

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[15] *Ann. Reports*, 1928, **25**, 261.

[16] *J. Physiol.*, 1929, **68**, 97; *A.*, 1930, 104.

[17] The vagus nerve belongs to the parasympathetic branch of the autonomic system.—J. P.

[18] *Biochem. J.*, 1929, **23**, 1064; *A.*, 1929, 1479.

[19] *J. Physiol.*, 1930, **70**, 109.

The Vitamins.

Carotin and Vitamin-A.—During the past year the main interest of investigators has centred on the problem of the relationship of the hydrocarbon carotin to vitamin-*A*. Earlier work in this field was reviewed in the Report of last year.[20]

There is now general agreement that carotin of the highest purity so far attained, and of whatever origin, possesses intense vitamin-*A* activity. T. Moore [21] has, for instance, shown that carotin prepared from the unsaponifiable matter of red palm oil was active in doses of 0·01 mg. per day when fed to rats. It has become equally clear that carotin is not itself vitamin-*A*. W. L. Dulière, R. A. Morton, and J. C. Drummond [22] have described a careful colorimetric and spectroscopic differentiation of carotin from the vitamin-*A* of cod-liver oil. They found that the blue colours produced in the antimony trichloride reaction were of slightly different shade, that of carotin being characterised by an absorption band at 590 $\mu\mu$, and that of vitamin-*A* by a band at 608—612 $\mu\mu$: in regard to the ultra-violet absorption spectra vitamin-*A* showed a band at 320—330 $\mu\mu$ which was absent in the case of carotin. Moreover, pure carotin, which is deeply coloured, possesses an activity not greatly exceeding that of the best cod-liver oil concentrates, which are at most of a pale orange colour. The inevitable conclusion seems to be that carotin is transformed into vitamin-*A in vivo.* Direct evidence of this transformation has been obtained by T. Moore [23] and by N. S. Capper.[24] Moore has shown that the liver oils of rats suffering from vitamin-*A* deficiency invariably gave negative results when tested with the antimony trichloride reagent. After such rats had been cured by the administration of large doses of carotin, it was found that traces of yellow pigment appeared in the liver oil. At least 99% of the chromogen present was vitamin-*A*, as characterised by (*a*) the absence of such intense yellow pigmentation as must have accompanied the storage of carotin as such; (*b*) an intensely positive antimony trichloride reaction showing a marked band at 610—630 $\mu\mu$; (*c*) the appearance of an absorption band in the untreated oil at 328 $\mu\mu$; (*d*) intense biological activity. Capper has shown that the band at 320—330 $\mu\mu$ is absent from the liver oils of rats suffering from depletion of vitamin-*A*, but is present in the liver oils of similar rats subsequently cured by massive doses of carotin. Since this band is absent from the absorption spectrum of purified carotin, it is deduced that the substance which is responsible for the presence of this band in the spectrum of the liver oils of carotin-treated rats has been synthesised *in vivo* from the carotin.

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[20] *Ann. Reports*, 1929, **26**, 245.

[21] *Biochem. J.*, 1929, **23**, 1267; *A.*, 1930, 255.

[22] *J. Soc. Chem. Ind.*, 1929, **48**, 518.

[23] *Biochem. J.*, 1930, **24**, 692; *A.*, 962.

[24] *Ibid.*, pp. 453, 980; *A.*, 822, 1321.

In view of the foregoing results and of the importance of butter as a source of vitamin-*A*, R. A. Morton and I. M. Heilbron [25] have investigated the presence of carotin and of the vitamin in this fat. Both were found to be present and to be capable of spectroscopic determination with some degree of accuracy. These workers support Moore's view regarding the conversion of carotin into vitamin-*A* *in vivo*. Further evidence bearing on this relationship has been published by H. von Euler, V. Demole, P. Karrer, and O. Walker,[26] who have determined the carotin and xanthophyll contents of the ether-soluble unsaponifiable matter of the extractives of the dry leaves of various plants, of the flowers of *Caltha palustris*, and of maize grains. In all cases the vitamin activity runs parallel with the carotin content. An interesting result is that of M. Javillier and L. Émerique,[27] who found that a preparation of carotin from spinach which had been kept in an atmosphere of hydrogen and exposed to feeble diffused light for 40 years exhibited the physiological properties of vitamin-*A*. The same workers [28] record the purification of a specimen of carotin of melting point 172—173° to yield one of melting point 184—185°. This was achieved by five successive purifications by dissolution in carbon disulphide, slow addition of the solution to boiling methyl alcohol, removal of the carbon disulphide, and filtration of the residual liquid, all operations being carried out in an atmosphere of nitrogen. The purified product retained its vitamin activity.

Vitamin-D.—The anti-rachitic vitamin continues to elude capture, but if anything the gap between the fugitive vitamin and its pursuers is narrowing. F. A. Askew, R. B. Bourdillon, H. M. Bruce, R. G. C. Jenkins, and T. A. Webster [29] have published a detailed study of the distillation of vitamin-*D*, or rather of the resins obtained by the removal of unchanged sterol from irradiated ergosterol. A specially designed still and a very high vacuum were employed. On three occasions the redistillation of one of the more volatile fractions yielded a crystalline product. Recrystallisation was possible and the material was obtained as rather thick needles showing conspicuous double refraction in polarised light. The melting point was 113—115°. In each case the crystals have shown very high anti-rachitic activity. The authors point out that, if there is only one substance possessing intense anti-rachitic activity, that is, only one vitamin-*D*, it is not very probable that these crystals are this substance. Resinous mixtures of approximately the same anti-rachitic activity as the crystals have frequently been obtained, although their low melting points and varying absorption spectra suggested that they were mixtures of a number of substances. The interest of this problem justifies a detailed reference to the four possibilities advanced by the authors. These are :

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[25] *Biochem. J.*, 1930, **24**, 870; *A.*, 1321.

[26] *Helv. Chim. Acta*, 1930, **13**, 1078; *A.*, 1624.

[27] *Compt. rend.*, 1930, **190**, 655; *A.*, 647.

[28] *Ibid.*, 1930, **191**, 226; *A.*, 1221.

[29] *Proc. Roy. Soc.*, 1930, [*B*], **107**, 76; *A.*, 1481.

(1) The crystals may be an inactive substance contaminated by traces of an intensely active oil deposited on their surfaces. This is not thought to be probable, since the cleanest specimen obtained showed the highest activity and appeared free from oil. If an oil film was the source of the activity, it must have had an activity of a higher order than any yet observed.

(2) The crystals may be a mixture in any proportion of two or more substances of sufficiently similar molecular dimensions to form homogeneous crystals, only one of them being vitamin-*D*. This is regarded as possible in view of the frequent occurrence of such mixed crystals among the sterols.

(3) The crystals may be a loose compound of an active and an inactive substance.

(4) There may be a number of radiation products of ergosterol all possessing high but unequal anti-rachitic activities, that is, a number of compounds any one of which could be called vitamin-*D*, but would cause only a fraction of the total activity of the ordinary irradiation products of ergosterol. This is regarded as not improbable.

It is observed that during the heating in a vacuum there is formed a new substance with intense absorption at 290 $\mu\mu$. This substance has no anti-rachitic activity, but its appearance is associated with the disappearance of the vitamin. It cannot be regarded as a simple product of vitamin destruction, since its production bears no direct relation to the vitamin content shown, before distillation, by the irradiation products from which it is formed. The two conditions which favour its formation and the concurrent disappearance of the vitamin are previous protection of the irradiation product from exposure to air, and the exclusion of short wave-lengths during the original irradiation. It is tentatively suggested, in explanation of these facts, that one of the initial irradiation products of ergosterol is an unstable substance with low absorption and no anti-rachitic activity, that this substance is very readily destroyed by absorption of oxygen, or by radiation of short wave-lengths, but that, if not previously destroyed, it is converted by heat into the substance absorbing light at 290 μμ with an associated destruction of part of the vitamin present.

The same authors in another paper [30] report the results of further irradiation of the radiation products of ergosterol. When the second irradiation was carried out with short rays (210—280 μμ) acting on the substances formed by a first irradiation with "long" rays (longer than 280 μμ), there resulted a large increase in absorption at 280 μμ and a decrease in anti-rachitic potency. On re-irradiation with long rays, the absorption at 280 μμ was slightly decreased, whilst the activity was unchanged. The substance with high absorption at 280 μμ can be formed by the action of short waves on some product of a previous action of long waves on ergosterol. The results show that the product with high absorption at 280 μμ is not vitamin-*D* as previously supposed,[31] and it is now suggested that the initial effect of long-wave radiation on ergosterol is the simultaneous production of at least two substances, only one of which is vitamin-*D*.

In the Report of last year reference was made to the condition of hypervitaminosis [32] induced by the administration of excessive doses of irradiated ergosterol or other source of vitamin-*D*. During the past year numerous investigations, which need not be detailed here, have been devoted to a consideration of this problem and much valuable information has been obtained. But in view of the foregoing discussion concerning the products of irradiation of ergosterol, a communication by F. Holtz and E. Schreiber [33] is significant. It is claimed that the hypervitaminosis effects, namely, calcium deposition, hypercalcæmia, hyperphosphatæmia, and circulatory deficiency, are produced by a toxic substance, which they call the "calcinosis" factor, and not by vitamin-*D* itself. The toxic factor and the vitamin produced under various conditions of irradiation are stated to be closely proportional. It is further claimed that the calcinosis factor may be isolated and its effects studied by heating the irradiated ergosterol to 160°, or by reduction with sodium in alcohol, whereby the anti-rachitic vitamin alone is destroyed.

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[30] *Proc. Roy. Soc.*, 1930, [*B*], **107**, 91; *A.*, 1481.

[31] *Ann. Reports*, 1929, **26**, 249.

[32] *Ibid.*, p. 251.

[33] *Z. physiol. Chem.*, 1930, **191**, 1; *A.*, 1481.

The B *Vitamin Group.*—Since the nature of the *B* vitamin complex was last dealt with in these Reports[34] the problem has undergone a further development in complexity. In 1928 R. R. Williams and R. W. Waterman[35] submitted evidence that polyneuritic pigeons, made so either by an exclusive diet of polished rice, or by a synthetic diet complete in all respects save for the vitamin-B complex, require for full weight restoration or maintenance a factor which is distinct in properties and distribution from the anti-neuritic vitamin-B_1, or the anti-pellagra vitamin-B_2. In 1929 V. Reader[36] presented evidence for the division of the B vitamin complex into three components, all necessary for the nutrition of the rat. It was shown that two of these were destroyed by autoclaving yeast extract at p_H 9 for one hour at 120°. It was later[37] found possible to concentrate two of these components, and it was then shown that the third must still be added to the diet of rats to enable these animals to grow to maximum adult size. The Williams–Waterman vitamin and the Reader vitamin are not the same, although they were both at first called vitamin-B_3 by their respective discoverers. The matter has now been amicably adjusted and the term B_3 is applied to the first-mentioned vitamin, and B_4 to the second. The present position may perhaps best be summarised in the following table :

Vitamin.	Required by growing rat.	Required by adult pigeon.	Properties.
B_1	+	+	Alkali-labile, the original anti-neuritic vitamin of Eijkmann, called torulin by Peters.
B_2	+	—	Alkali-stable, the anti-pellagra vitamin of Goldberger, also called the anti-dermatitis vitamin.
B_3	—	+	Thermo-labile, the Williams–Waterman pigeon factor.
B_4	+	+	Alkali-labile, the rat factor of Reader.

W. H. Eddy, S. Gurin, and J. Keresztesy[38] have extended the original work of Williams and Waterman and find that yeast, whole grains, and malt are good sources of vitamin-B_3, but while malt extract often retains a good concentration of B_1, its method of manufacture practically eliminates B_3. Malt extracts made at temperatures as low as 60° are practically devoid of B_3, although they are still very effective as sources of B_1. Beef and beef liver are fair sources of B_3 and distinctly superior to milk, orange- and tomato-juice, spinach, and potato-juice or cane molasses in this respect. Vitamin-B_3 is much more heat-labile than B_1, and, if it is submitted to alkali treatment before drying, temperatures as low as 20° will markedly reduce the content of this vitamin in yeast. Miss Reader obtains vitamin-B_4, the second alkali-labile rat factor, from the mercuric sulphate precipitate in the Kinnersley and Peters process [39] for vitamin-B_1. In this precipitate some 75% of the original B_4 is recovered. It is suggested that the vitamin forms an insoluble mercury salt, or a double salt with mercuric sulphate.

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[34] *Ann. Reports*, 1928, **25**, 269.

[35] *Ibid.*, p. 269.

[36] *Biochem. J.*, 1929, **23**, 689; *A.*, 1929, 1203.

[37] *Ibid.*, 1930, **24**, 77; *A.*, 380.

[38] *J. Biol. Chem.*, 1930, **87**, 729; *A.*, 1222.

In regard to the *B* vitamin components of longer standing than those just discussed, B. C. Guha and J. C. Drummond,[40] and B. T. Narayanan and J. C. Drummond [41] describe new methods of concentrating B_1 and B_2 respectively. R. R. Williams, R. E. Waterman, and S. Gurin [42] have applied the process of Jansen and Donath for B_1 to brewers' yeast, but have failed to isolate highly active material. On applying the method as did the original authors to rice polishings, general confirmation of the Dutch results was obtained, although the yield of active material was much lower and crystals could not be obtained. The authors' highly purified but amorphous preparations behave in all respects like the crystalline substance of Jansen and Donath. These results are therefore similar to those obtained by Kinnersley and Peters in 1927.[43] It may be mentioned that B. C. P. Jansen [44] has published further improvements in his methods of fractionating the extracts of rice polishings.

Bios.—In a paper published by B. T. Narayanan [45] the non-identity of " bios " with vitamin-B_2 is established, and J. G. Davies and J. Golding [46] have made a similar finding with regard to vitamin-B_1. A. M. Copping [47] has shown that the need for " bios " depends on the type of yeast and on the nature of the culture medium. The need is probably related to the fermentative activity of the yeast. Some of the highly cultivated brewers' yeasts will not grow in a purified glucose–salt medium without the addition of small amounts of extracts containing an organic " bios." Narayanan describes a method of fractionation which provides concentrates producing marked stimulation of yeast growth in doses of the order 0·01 mg. per c.c. of an artificial sugar–salt medium. The final concentrate appears to consist largely of relatively simple nitrogenous substances and contains no phosphorus. No evidence in support of the complex nature of " bios " was obtained in the course of these investigations, nor is there any indication that inositol is an essential unit of " bios."

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[39] *Biochem. J.*, 1927, **21**, 778.

[40] *Ibid.*, 1929, **23**, 880; *A.*, 1929, 1496.

[41] *Ibid.*, 1930, **24**, 19; *A.*, 380.

[42] *J. Biol. Chem.*, 1930, **87**, 559; *A.*, 1222.

[43] Harben Lectures, *J. State Med.*, 1930, **38**, 38.

[44] *Rec. trav. chim.*, 1929, **48**, 984.

[45] *Biochem. J.*, 1930, **24**, 6; *A.*, 375.

[46] *Ibid.*, p. 1503; *A.*, 1479.

[47] *Ibid.*, 1929, **23**, 1050; *A.*, 1929, 1491.

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GEOCHEMISTRY.

THE year's literature has reflected a substantial increase in interest in almost all branches of geochemistry. There are considerable improvements in the study of opaque ores by reflected light, which seem destined to stimulate interest in these substances and to remedy the somewhat one-sided development of the science in favour of the non-opaque minerals. *X*-Ray researches on most of the chief mineral groups have already been published, and there is a consequent slackening in the description of entirely new structures; many of the postulates on which these have been based are now receiving more rigorous examination, an outstanding feature being the better investigation of solid solutions and a clearer realisation of the difficulties that arise from the fact that material in solid solution cannot be detected by the ordinary methods of *X*-ray analysis. Mineral synthesis includes investigations in groups such as the sulphides and iron ores, beside the extension of work on the oxide systems. In the description of mineral species many new names will be found, and a welcome feature is the greater completeness of the descriptions and analyses; special mention may be made of the investigation of phosphate minerals which forms part of research work assisted by Harvard University, and published in the *American Mineralogist*. Many chemists have obtained materials for research from the well-known "Ward's Natural Science Establishment," now connected with Rochester University; in the autumn of 1930 this valuable mineral collection was partly destroyed by fire, but fortunately much of the stock has been saved so that the interruption in supplies may not be so serious as was at first feared. Many mineral descriptions will be mentioned in the following pages; attention may perhaps be directed to the descriptions of the opaque sulphides, phosphates, felspars, and clays, in which considerable advances have taken place. It has been impossible to include a review of all branches of the subject; for many important researches on the properties of minerals, rock analyses, etc., reference must be made to the "Abstracts" or to the literature.

Mineragraphy.

This name seems destined to come into general use to designate the study of minerals under the microscope by reflected light. Although the practical development of this subject has taken place mainly during the past few years, it is already clear that in its own sphere the subject will rival in importance metallography and the study of transparent rock sections. Probably the most important line of development in mineralogy at the present time, its possibilities may already be gathered in some degree from the excellent photomicrographs to be found, for example, in the current volume of *Economic Geology*. Methods of examination by etching, by polarised light in the manner initiated by J. Konigsberger, and by hardness and other tests, are rapidly being reduced to standard laboratory practice, for which text-books are already available. Metallographers have long been accustomed to study and even to build up a phase-rule diagram from the microstructure of the corresponding alloys, and similar, though generally less adequate, attempts have been made at the more difficult task of interpreting the microstructure of rocks in terms of the chemical data available. In the same way the present method has greatly helped in the investigation of the chemical history of sulphide and oxide ore-bodies. Important among these are the sulphide ores of Cobalt, Ontario, which have been studied by E. Thompson;[1] etching methods are developed in detail for the nine chief arsenical minerals, and ore from the several mines is examined with special reference to the relation between the composition and the distance from a diabase sill which is regarded as the source of the mineralisation. A. M. Bateman[2] contributes an examination of the copper ores of Rhodesia. These are bedded sandstone or clay, with minute disseminated grains of chalcocite, bornite, or chalcopyrite, and lying near the base of the Roan Series; oxidation is widespread near the surface. All the rocks show signs of heat alteration, possibly by hot solutions carrying the ores. Linnaeite (Co_3S_4) has been found in several mines; it contains innumerable minute veinlets of other sulphides—an instance of the importance of examining opaque minerals by the present methods before interpreting their analyses. Chalcopyrite occurs alone or in intergrowths with bornite, which exhibits an anomalous anisotropic form. Chalcocite is the most important mineral; it exists in two forms, that originating above 91° being cubic; detailed study of the intergrowths suggests that the structures are of isometric form and that much of the ore was deposited by hot solutions, contrary to the general opinion that this ore is " supergene."

H. Borchert[3] describes with many photomicrographs the etching, chemical characteristics, and association of the tellurides, for which it is suggested that the transition point of hessite at 150° would afford a " geologic thermometer."

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[1] *Econ. Geol.*, 1930, **25**, 470.

[2] *Ibid.*, p. 365.

[3] *Jahrb. Min., Beil.-Bd.*, 1930, [*A*], **61**, 101.

Contributions to theory and methods include an account of the diamond saw, by J. W. Vanderwilt,[4] and a description of special methods for preparing " thinned " polished sections for examination by either method of illumination.[5] Accurate measurement of the reflecting power plays an important part in the identification of ore minerals; H. Frick [6] describes the use of a reflexion photometer ocular; this instrument permits a comparison of the reflected light with the intensity of the incident beam, part of which is deviated through prisms to the ocular. The general problem of ascertaining the crystallographic directions in a surface under reflected light is discussed by K. Chudoba.[7] In the case of many opaque ores to be mentioned below, the description is accompanied by an investigation by mineragraphic methods, which may now be regarded as essential in all but the simplest cases.

Synthesis and Decomposition.

Among the oxide systems that for wollastonite–anorthite–pyroxene has been determined by L. Koch.[8] Quickly cooled melts were studied optically; the resulting triangular diagram is of fairly simple character, complicated by the separation of the two forms of $CaSiO_3$ and of the compound $5CaO,2MgO,6SiO_2$ in a narrow field. This system is of great technical importance for blast-furnace and similar slags, to which reference is made. N. L. Bowen, J. F. Schairer, and H. W. V. Willems [9] have investigated the ternary system Na_2SiO_3–Fe_2O_3–SiO_2, by the method of quenching. Acmite, one of the three ternary compounds that crystallise, decomposes on melting, yielding hæmatite; the sinking of these heavy crystals would yield a great variety of residual melts according to the extent of the differentiation. The lowest eutectic is rich in silica and crystallises below 800°, so that quartz is formed directly from the melt, even in the absence of mineralisers.

For the study of ores much interest centres in the sulphide reactions, and a considerable body of research on that subject is now in progress. Sulphide replacement has been studied experimentally by J. C. Ray.[10] Bornite forms finely divided graphic structures with chalcocite, and these can be " dispersed " to a uniform texture by heating to 150° in balsam, while with steam this temperature was brought down to 100°. Vessels of Pyrex glass were next used at 100°, and by the introduction of reagents a number of metasomatic reactions were accomplished; the resulting structures are illustrated by photographs in reflected light.

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[4] *Econ. Geol.*, 1930, **25**, 222.

[5] J. D. H. Donnay, *ibid.*, p. 270.

[6] *Jahrb. Min.*, *Beil.-Bd.*, 1930, [*A*], **61**, 31.

[7] *Centr. Min.*, 1930, [*A*], 14.

[8] *Jahrb. Min.*, *Beil.-Bd.*, 1930, [*A*], **61**, 277.

[9] *Amer. J. Sci.*, 1930, [v], **20**, 405.

[10] *Econ. Geol.*, 1930, **25**, 433.

An outstanding problem is that of the origin of the siliceous iron ores of the Lake Superior region. In a valuable research, J. W. Gruner[11] shows that silica is soluble in hot distilled water to a degree not hitherto realised. Various forms of silica were heated with water in gold-lined bombs; at 300°, the amount dissolved reached about 1000 parts per million, greatly in excess of the value at 200°. Silicates did not yield so strong a solution, possibly because of the presence of the metal ions. Oxidised Lake Superior ores are now known to exist at depths of several thousand feet, and Gruner suggests that the oxidation is due to thermal waters and not, as hitherto supposed, to atmospheric waters. This view is supported by detailed tests on the oxidation of ferrous minerals, which takes place readily in a current of steam at 200°. Magnetite is not oxidised so rapidly, and in some bomb experiments magnetite was formed by the limited oxidation of siderite. The second part of the paper contains a description of the principal deposits in the Lake Superior region; their formation is attributed to hydrothermal reactions due to the injection of enormous basic magmas under pre-existing iron formations.

Corundum and carborundum are prepared for use as abrasives; their synthesis has been described by V. L. Eardley Wilmot.[12] Artificial periclase is also prepared commercially and is a valuable, though expensive, insulating material. Silica clinkers, formed during forest fires, have sometimes been regarded as meteorites; D. T. Englis and W. N. Day[13] have analysed a variety of samples which disprove this mode of origin. F. Machatschki[14] has studied "synthetic domeykite," which appears to be a mixture of two arsenides that yield true synthetic domeykite after melting; algodonite and whitneyite[15] yield on fusion Cu_3As and metallic copper.

Great interest attaches to the alterations produced in minerals by heating or chemical treatment. H. Haraldsen[16] describes the changes produced in talc on heating. O. Tamm[17] has shown that on prolonged grinding felspar is attacked by water, yielding an alkaline solution while the particles become hydrated.

Publications from the Geophysical Laboratory at Washington[18] comprise work on the oxide systems including leucite-diopside, acmite, potassium metasilicate, the cristobalite liquidus, and Na_2O-SiO_2. Vulcanicity is represented by studies on the gases evolved in the Valley of 10,000 Smokes, Katmai, and on the Central African volcanoes. Several inorganic systems have been examined including the polymorphous forms of sodium sulphate and potassium nitrate, the ferrites of magnesium, zinc, and cadmium, and the behaviour of nitrogen pentoxide at low pressures. Further progress has been made in determining the elasticity of rocks and minerals [19] and the physical properties of silica, and thermodynamic studies bearing on geochemistry include work on the solutions water–ammonia and an extensive discussion of the equations governing multicomponent systems. Two papers deal with petrology, on pacificite and the St. Pauls Rocks, and one with the Mid-Atlantic ridge. Corresponding work during the preceding year is given in abstract in the Annual Report of the Director [20] for 1929.

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[11] *Econ. Geol.*, 1930, **25**, 697, 837.

[12] Canada Dept. of Mines, " Abrasives," Pt. IV, Ottawa, 1929.

[13] *Science*, 1929, **69**, 605; *A.*, 1929, 1418.

[14] *Centr. Min.*, 1930, [*A*], 19.

[15] *Centr. Min.*, 1929, [*A*], 371; *Chem. Zentr.*, 1930, i, 957; *A.*, 1017.

[16] *Jahrb. Min., Beil.-Bd.*, 1930, [*A*], **61**, 139.

[17] *Chem. Erde*, 1930, **4**, 420; *A.*, 315.

[18] Full references to these papers are included in the postcard lists, Nos. 50—53, circulated by the Laboratory during the year.

X-*Rays and Chemical Constitution.*

For the geochemist, the silicates possess an outstanding interest, and the year has been distinguished by an unusual number of papers dealing with the chemical formulation of the silicates in the light of *X*-ray research. The complete novelty and importance of the *X*-ray method of crystal measurement led temporarily to a quite abnormal output of descriptive work; with the result that, for the silicates in particular, the general examination of the structures is now approaching completion. Valuable summaries by W. L. Bragg of this work on the silicates were mentioned in last year's Report, and a further very complete account by the same author has appeared during the current year.[21] This summary is of special interest on account of the light it sheds upon the value of the proofs offered for the proposed silicate structures. The brief indications given make it quite clear that some of the more complex silicates have been interpreted by means of principles which are not uniform and possess a rather alarming degree of elasticity. Thus for sillimanite we learn that " the substitution of aluminium for silicon will not affect the *X*-ray diffraction," and that " the removal of one atom of oxygen in forty appears to be tolerated without spoiling the structural scheme "; in Taylor's solution for analcite " sixteen sodium atoms must be distributed between twenty-four positions in the unit cell." In ultramarine, on the other hand, Jaeger has a surplus of sodium atoms, and these are disposed of by assigning them to " wandering " positions in the unit cell. Attention has already been drawn in previous reports to certain inconsistencies between the proposed structures and the actual chemical composition of the substances concerned; a closer agreement is much to be desired. Future work may be expected to deal to an increasing degree with the more difficult and debatable aspects of the subject. It would lie outside the scope of the present report to give details of the highly complex structures themselves; claims have been made that the chemical properties of a substance can be predicted from the form of the space-lattice, but present achievements in this direction can hardly be said to have practical importance for the chemist, who will still find it necessary to determine melting points and solubilities by the usual methods. One aspect of the subject, however, seems likely to receive much attention from geochemists in the immediate future; this is the question how far *X*-ray data can be used to ascertain the true chemical formulæ of the silicates.

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[19] *Proc. Nat. Acad. Sci.*, 1929, **15**, 713.

[20] Carnegie Inst. Wash., Year Book, No. 28, 1929, p. 67.

[21] *Z. Krist.*, 1930, **74**, 237.

Formulation of the Silicates.

In complexity and numbers, the silicates as a class challenge comparison with the organic compounds, and many attempts have been made to devise corresponding chemical formulæ. On the introduction of *X*-ray analysis, a curious reaction set in against the use of formulæ of any kind, for it was discovered that the atomic spacings showed in general no demarcation between atoms that might be expected to belong to neighbouring molecules. Students of organic chemistry had, it is true, been warned of the danger of attributing any special physical significance to the " bonds " of a structural formula, and it was well known that some constitutive properties, such as the spectrum of the uranyl group, were present equally in the crystalline state. Yet the anticipation that chemical " bonds " would be evidenced by some physical union between the atoms was so strong that attempts at formulation were very generally abandoned; P. Groth himself was led to announce " it is now no more a question of the chemical molecule." Of late years the tendency has been to resume the search for a chemical theory of the silicates. The absence of molecular demarcation is now known to be very general in crystals even of the most neutral chemical character, in which there is every reason to think the atoms are chemically combined: it is difficult, for example, to believe that the molecules of a high explosive undergo any serious disturbance during crystallisation. Characteristic groups of atoms of the kind to be expected from the chemical formulæ have now been recognised both in organic compounds and in the silicates: the crystalline structure in both classes of compound suggests that atoms combined together must remain in association, but are capable of a limited free movement around one another so as to assume stable symmetrical positions in a close-packed space-lattice. The chemical molecules might be regarded, in a crude analogy, as readily flexible, but not usually subject to decomposition on entering a space lattice.

In considering the very interesting formulæ proposed by Machatschki and others,[22] it may be well to note briefly a somewhat misleading tendency in present-day nomenclature. The properties of the space-lattice have been explained in terms of many new concepts, based, of course, upon the *X*-ray properties of the crystal. There has been, however, a seeming reluctance to introduce corresponding new terms; enthusiasm for the application of *X*-ray methods to chemical problems has led those concerned to apply old-established chemical terms, such as "valency," "ion," "stereochemistry," and "formula" in a sense quite outside their established use in chemistry. Pauling, for example, has introduced the term valency to designate a vague and often fractional atomic property which is held to govern the grouping of atoms in the space-lattice. Again, it has been held that the atoms in a space-lattice are in the "ionised" state; the term "ion" has consequently been quite commonly used even in cases where the question of ionisation is not under discussion, and where the less debatable term "atom" would more accurately represent the concept involved. The idea of ionisation in crystals seemed at first to derive support from a well-known estimate of the size of oxygen, due to Wasastjerna. That author extrapolated the atomic volumes for a salt in solution so as to obtain an estimate of the volumes of the atoms after crystallisation. In accordance with the theories current at the time, he represented the atoms as spheres and calculated the corresponding "ionic" radii for chlorine, etc. This estimate has since been used as a basis for the calculation of many "ionic radii," and P. Niggli, in the introduction to his latest work on the properties of binary compounds, has summarised the current position as follows: [23]

"Now experiment shows that radii so calculated are in no way constant; many of the results vary according to the substance chosen for starting the calculation. Again, it must not be assumed that the practice of dividing the interatomic distance into atomic domains is advantageous for exhibiting the relation between the crystalline state and that of free ions. The discrepancies between calculated and observed interatomic distance, which lead to inconstancy of the radii, may be ascribed to polarisation, deformation, contrapolarisation, structure-incommensurability, etc.; but it is clear, to anyone who calculates the radii by way of some other hypothesis, how much all these concepts depend upon basic postulates whose arbitrary nature cannot be evaded.

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[22] These discussions have appeared chiefly in the pages of the *Zeitschrift für Kristallographie*, 1930, **73–75**, and of the *Centralblatt für Mineralogie*, Abt. *A*, 1930. Formulæ have been advanced for the contents of the unit cell in a number of the most complex minerals; for details, reference should be made to these volumes.

[23] *Z. Krist.*, 1930, **74**, 375 (somewhat condensed in translation).

"The consistent and comprehensive system [of atomic radii], developed by L. Pauling, H. Grimm, and especially V. M. Goldschmidt, covers a wide range of phenomena in crystal structure. Anyone who has reconciled himself to the fundamental postulates may usefully employ the system for crystallo-chemical problems; but it must be clearly understood that the regular relationships so described are in themselves no evidence for the correctness of the hypothesis. In fact it is possible to discover the same regular relationships, and even more extensive ones, without postulating this division into atomic radii, which is inevitably of an arbitrary character. It can be done in a second way."

Niggli then discusses the relations between interatomic spacing and the nature of the elements present; like many other properties, the spacing varies periodically with the atomic weight, and relationships of a general character can be traced. For this subject he employs the name stereochemistry, but in a sense very different indeed from that in which the word is used by organic chemists.

Lastly, to return to the subject of the present note, the word formula * has been used to designate the contents of the smallest repeated unit in the space-lattice. Such a group of atoms can be represented by symbols like an ordinary chemical formula, indeed in many simple substances the two are identical. But in substances with more complex chemistry the two no longer stand in any necessary relationship. It will be convenient, in the present discussion, to use the terms "physical formula" for the above unit group and "chemical formula" for the symbols that summarise the composition and reactions of the compound in question. The difference between the two kinds of formula has given rise to much confusion because so many physical formulæ are written with substitutions, like (Ca,Na), that violate the rules of valency governing the construction of a chemical formula.

The importance of the physical formula lies in the fact that it is this, and not necessarily the chemical formula, that is obtained when the structure is solved by *X*-ray methods. If all the points of a given kind in the space lattice were occupied by like atoms, the relation to the chemical formula would be simpler: the discrepancy arises chiefly from the fact, now well established, that atoms of similar volume may "proxy" for one another in the lattice; for instance, sodium may occupy the place of a calcium atom. This kind of substitution is represented in the physical formula by the group (Na,Ca) in the same way as an isomorphous replacement in a chemical formula, but the two must be clearly distinguished.

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* Machatschki uses the term crystallo-chemical formula.

Substitution over the full range implied in the physical formula would obviously yield a number of compositions which are known to have no stable existence: the fact is that only those physical substitutions are possible in which the resulting difference in chemical valency is compensated by a change in the composition of the rest of the crystal. The nature of this compensation depends on the chemistry of the compound, and the physical formula may shed little or no light on the problem.

The Spinels.—The serious limitations of the physical formula are well illustrated by the case of the spinels, reviewed in a very interesting paper by F. Machatschki.[24] A typical spinel has the formula $(Mg,Fe)O,Al_2O_3$. Now titaniferous spinels are known, in which a chemical molecule, probably RO,TiO_2, enters in solid solution; *X*-ray analysis shows that the titanium occupies the place of aluminium, so that Machatschki writes the *physical* formula of the spinel group so far defined as $Y\,Y'_2\,(O,F)_4$, where Y represents atoms Mg,Fe,Zn, etc., and Y' is Al,Fe,Cr,Ti, etc. But this is not all, for there are yet other spinels with a wider range of composition: a series of synthetic crystals has been prepared which are, chemically speaking, solid solutions of free alumina in ordinary spinel. Aluminium atoms here occupy the place of magnesium, and the physical formula must now be further simplified, so that it assumes the form Y_3O_4, where Y now means (Mg,Fe, etc.; Ti,Al,Cr, etc.). Machatschki does not further pursue these developments, but it seems fair to remark that another step is probable, if not already necessary: The Y elements do not differ very widely in volume from oxygen, and if by any chance conditions should be realised in which one of them could replace oxygen in the space-lattice the physical formula would undergo another, and presumably final, simplification into the form Z_7 where Z might be any atom. Thus the increasing complexity of this series of compounds, judged from the chemical standpoint, is met, not by a corresponding development in the scope and diversity of the physical formula, but by its almost complete disappearance into the vaguest of generalities. Clearly, the *X*-ray analysis of such a complex group, yielding the formula Z_7, would shed very little light upon the chemical formulæ of the well-known compounds present.

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[24] *Centr. Min.*, 1930, [*A*], 191.

Minerals.

Elements.—The generally accepted theory that the gold deposits of the Rand conglomerate were formed as placer deposits has been examined by L. C. Graton,[25] who gives a very full discussion of the evidence. On the grounds of the absence of detrital grains of gold and other heavy minerals, the fineness of the grain size, enrichment of the top as well as the bottom of some reefs, and the prevalence of auriferous quartz veins, he concludes in favour of hydrothermal origin, from solutions infiltrating the conglomerate. C. D. Hulin [26] describes an unusual gold vein from California, in which the gangue mineral is largely apatite. Diamond deposits on the Upper Araguaya River have been described by F. W. Freise; [27] and those on other Brazilian fields by A. P. L. Bétim.[28] Perhaps the most famous deposits in the world at present are the raised beaches near the mouth of the Orange River in South-West Africa. These are briefly described by A. L. Dutoit; [29] the diamonds are concentrated along the foot of the ascending storm beach at the inner side of the raised beach terrace; by means of carefully contoured maps, a succession of raised beaches has been traced, and the productive area has been rapidly extended, so as to indicate some wider source than the Orange River itself.

Curtisite,[29a] a new hydrocarbon, has the formula $C_{24}H_{18}$. Thucholite [29b] is interesting on account of its occurence with uraninite.

Halides.—Detailed mineral analyses of the Solikamsk salt deposit in Russia are given by J. V. Moratschevski; [30] N. N. Efremov and A. A. Veselovski [31] discuss the bromine content of the carnallites; I. V. Poiré [32] finds that their colour is due to iron oxide as needles, threads, and platelets. Sodium chloride and sylvite preceded the other salts, and G. G. Urazov [33] has discussed the order of crystallisation, which agrees with that in the quaternary system $KCl-NaCl-MgCl_2-H_2O$. Red salt from the southern United States was also found by J. E. Tilden [34] to contain matted tubules mingled with iron oxide; they appear to be the remains of an organism for which he proposes the name *Phormidium antiquum.* One of the most striking occurrences of rock salt is the exposed salt plugs of Southern Persia, described by J. V. Harrison;[35] the salt has here been extruded on a large scale, and even forms "glaciers" that spread outward over the surrounding rocks.

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[25] *Econ. Geol.*, 1930, May (supplementary volume).

[26] *Ibid.*, p. 348.

[27] *Ibid.*, p. 203.

[28] *Bull. Soc. franç. Min.*, 1929, **52**, 51; *A.*, 1930, 1016.

[29] *Econ. Geol.*, 1930, **25**, 653.

[29a] *Amer. Min.*, 1930, **15**, 169.

[29b] *Ibid.*, p. 499.

[30] *Ann. Inst. Anal. Phys. Chem.*, 1930, **4**, 113; *A.*, 1015.

[31] *Ibid.*, p. 99; *A.*, 1015.

[32] *Ibid.*, p. 85; *A.*, 1015.

[33] *Ibid.*, p. 41; *A.*, 1016.

[34] *Amer. J. Sci.*, 1930, [v], **19**, 297; *A.*, 570.

Sulphides and Sulpho-salts.—A remarkable occurrence of copper ores in Alaska is described by S. G. Lasky.[36] The deposit is mainly chalcocite, which proves on mineragraphic investigation to be of the isometric (high-temperature) form. It occasionally exhibits banded structures which are believed to indicate deposition in a colloidal form above 90°; this contained dissolved covellite which separated on cooling. Chalcopyrite, usually a vein-mineral of rather late formation, is found in Montana [37] in a magmatic deposit which is really a perthitic syenite composed mainly of orthoclase and albite; platinum is present with the copper. Graphic intergrowths of the chalcopyrite and niccolite from Sudbury, Ont., are described by C. Lausen,[38] who concludes that the first deposit of gersdorffite and quartz was shattered, with the introduction of maucherite followed by niccolite; chalcopyrite then replaced the niccolite. The word "graphic" has been used to describe a variety of inter-penetrant structures, due variously to simultaneous crystallisation from the melt, to "unmixing" of a solid solution and to replacement; in the present case, although it is known that the two minerals are mutually soluble at high temperatures, and "unmix" on cooling, the author holds that the structures are due to replacement.

W. H. Newhouse and G. H. Flaherty [39] have undertaken a comparison between various types of the metamorphic copper ores; these offer one of the most difficult geochemical problems, for it is hard to distinguish between deposits altered by the metamorphism and those due to chemical replacement of different mineral bands in the schist.

D. F. Hewett and R. N. Rove [40] describe veins exhibiting the sequence rhodonite, alabandite, and rhodocroisite, the last in part replacing the earlier minerals. The position of molybdenite in the sequence of deposition is dealt with by A. F. Buddington,[41] who describes a pegmatite from Alaska in which sulphides replace silicates in the sequence pyrite, sphalerite, pyrrhotite, chalcopyrite, molybdenite, followed by a zeolitic phase. W. F. Foshag and M. N. Short [42] have proved by mineragraphic examination that a mineral from Czechoslovakia with the composition of arsenoferrite,

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[35] *Quart. J. Geol. Soc.*, 1930, **86**, 463.

[36] *Econ. Geol.*, 1930, **25**, 737.

[37] *Bull. U.S. Geol. Survey*, 1929, **811**, [*A*], 50.

[38] *Econ. Geol.*, 1930, **25**, 356.

[39] *Ibid.*, p. 600.

[40] *Ibid.*, p. 36.

[41] *Ibid.*, p. 197.

[42] *Amer. Min.*, 1930, **15**, 428.

FeS_2, is isotropic; arsenoferrite is thus a true species distinct from löllingite. A similar investigation of an arsenical ore from Silesia is given by H. Schneiderhöhn.[43] Violarite and other nickel sulphides have been investigated by M. N. Short and E. V. Shannon,[44] who find that violarite from Sudbury, Ont., is identical with a nickel sulphide observed in several other ores with the formula $(Ni,Fe)_3S_4$. The well-known sulphide minerals of Hungary have been described by S. Koch,[45] who gives a method of analysis with descriptions of many bismuth and tellurium minerals. Nagyagite (analysed), proustite, and xanthoconite are described by L. Tohody.[46] Other complex sulphides include miargyrite from California (E. V. Shannon),[47] *antamokite*,[48] a new gold silver telluride from the Philippine Islands, *fülöppite*, $3PbS,4Sb_2S_3$, a new mineral from Hungary (I. de Finály and S. Koch),[49] and *ramdohrite*, $Ag_2S,3PbS$, a new mineral from Bolivia, described by F. Ahlfeld.[50] D. Guisen [51] has made a mineragraphic study of the sulpharsenites from the Binnenthal.

Oxides.—Much interest has centred in the occurrence of cassiterite. The question how far the Bolivian tin deposits are due to oxidation of sulphides continues to be debated; J. T. Singewald [52] holds that the greater part is hypogene. Details of the crystal habit of several types of cassiterite are given by F. Ahlfeld,[53] who gives lists of the occurrence of Bolivian sulphides and concludes against the downward migration of tin oxide. After quoting historical records, J. Hulmaier [54] gives an elaborate description of the crystal habit of cassiterite from the chief known localities. An instructive example of the origin of primary tin veins is recorded by D. R. Derry,[55] who describes a pegmatite in which the segregation of cassiterite-bearing streaks has occurred towards the hanging wall during consolidation of the rock.

Silica.—The name *lechatelierite* is proposed for natural fused silica, of which a remarkable occurrence is described by A. F. Rogers; [56] at Meteor Crater (Coon Butte), Arizona, layers of silica glass up to 6 inches in thickness are found at the bottom of the depression; these are attributed to fusion of the sandstone on impact of the meteorite. Agate has been studied by H. Heinz,[57] who gives analyses of the separate layers in flints from the chalk; artificial colouring affected the layers containing most opal. F. A. Burt [58] describes capsular silica from Texas. Quartz has been examined by R. Weil,[59] who finds that sections cut perpendicular to the axis indicate the existence of two types distinguished by optical properties and etch-figures. Among other oxides, the emery deposits at Peekskill are discussed by J. L. Gillson and J. E. Kama,[60] who regard the deposits as due to the reaction of magmatic solutions on the already consolidated margins of a norite mass, and on the surrounding metamorphosed schist, which is stated to have an acid composition. Cobalt minerals, including a new mineral *stainierite*, $(Fe,Co,Al)_2O_3,H_2O$, from Katanga, are analysed by V. Cuvelier.[61] Chromite is found in its purest form in meteorites; the ore-mineral varies widely in composition (L. W. Fisher).[62] E. S. Sampson and C. S. Ross [63] describe occurrences which they believe to indicate that chromite can be deposited at a late stage in mineralisation. Boehmite, Al_2O_3,H_2O, occurring as minute crystals in bauxite, is shown by R. Hocart and J. de Lapparent [64] to be homologous with lepidocrocite. Titanium in bauxite is shown by the latter [65] to occur always as a dust of highly refractive titanium minerals. Among the oxides of iron, mention may be made of pisolitic iron ores from Württemberg, which are regarded by E. A. Ehmann [66] as " fossil laterites," while M. Solignac [67] describes a limonite oolite from Tunisia with pellicles of phosphate. Manganese oxide is sometimes deposited along with limonite by spring waters, but there is usually a tendency for one or other mineral to predominate; examples are described by (Frl.) G. Schrenckenthal [68] in the cementation of gravels from the Marchfeld, while H. Lasch [69] gives an account of manganiferous nodules dredged from the bed of a lake in Upper Austria. Details of the oxides of manganese, with their occurrence and commercial uses, are given by E. Donath and

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[43] *Chem. Erde*, 1930, **5**, 385; *A.*, 733.

[44] *Amer. Min.*, 1930, **15**, 1; *A.*, 1551.

[45] *Bán. Koh. Lapok*, 1929, **62**, 425; *Chem. Zentr.*, 1929, ii, 2872; *A.*, 1930, 734.

[46] *Centr. Min.*, 1930, [*A*], 117.

[47] *Proc. U.S. Nat. Mus.*, 1929, **74**, No. 21; *A.*, 1930, 1397.

[48] *Philippine J. Sci.*, 1930, **41**, 137.

[49] *Min. Mag.*, 1929, **22**, 179; *A.*, 1930, 189.

[50] *Centr. Min.*, 1930, [*A*], 365.

[51] *Bull. Acad. Sci. Roumaine*, 1929, **12**, No. 7—10, 44.

[52] *Econ. Geol.*, 1930, **25**, 91, 211.

[53] *Ibid.*, p. 546.

[54] *Jahrb. Min., Beil.-Bd.*, 1930, [*A*], **61**, 403.

[55] *Econ. Geol.*, 1930, **25**, 145.

[56] *Amer. J. Sci.*, 1930, [v], **19**, 195.

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[57] *Chem. Erde*, 1930, **4**, 501.

[58] *Amer. Min.*, 1929, **14**, 222; *A.*, 1930, 187.

[59] *Compt. rend.*, 1930, **191**, 270; *A.*, 1155.

[60] *Econ. Geol.*, 1930, **25**, 506.

[61] *Natuurwetensch. Tijds.*, 1929, **11**, 170; *A.*, 1930, 188.

[62] *Amer. Min.*, 1929, **14**, 341; *A.*, 1930, 570.

[63] *Econ. Geol.*, 1930, **25**, 219.

[64] *Compt. rend.*, 1929, **189**, 995; *A.*, 1930, 189.

[65] *Ibid.*, 1930, **190**, 1312; *A.*, 886.

[66] *Chem. Erde*, 1930, **6**, 117; *A.*, 1397.

[67] *Compt. rend.*, 1930, **191**, 107; *A.*, 1156.

[68] *Chem. Erde*, 1930, **6**, 51; *A.*, 1398.

[69] *Tsch. Min. Petr. Mitt.*, 1930, **40**, 294; *A.*, 448.

H. Leopold.[70] Magnetite has been found by E. L. Perry [71] in the unusual form of fibrous veins, with granular magnetite at the centre; these occur in serpentine and are believed to be due to the replacement of asbestos. Jasper [72] containing magnetite and hæmatite has been described from the metamorphic iron ores of Wyoming.

Silicates.—Fibrous emerald-green actinolite (smaragdite), described by E. Harbich,[73] occurs with chromite and magnesite in serpentine from Serbia. Anthophyllite fibre from California described by J. D. Laudermilk and A. D. Woodford [74] proves to contain 7·4% Na_2O and is thus a new variety; it is fusible, but resists acid. Reference may be made here to the asbestos (chrysotile) of Shabani, South Africa, which has been described by F. E. Keep.[75] Another amphibole, blue-green in colour, from the Minnesota iron formation, is described by S. Richarz; [76] it contains 11·15% Al_2O_3, 7·92% Fe_2O_3, 1·67% Na_2O; this composition lies outside the amphibole formulæ recently advanced by Warren and Pauling, and to meet the difficulty two new additional constituent formulæ are proposed by Winchell.

Spodumene deposits in Dakota are described by G. N. Schwartz,[77] while C. Palache, S. C. Davidson, and E. A. Goranson [78] describe the hiddenite deposit of N. Carolina, which they regard as an example of pegmatitic mineralisation in three successive stages, the second pegmatite injection carrying the lithia minerals, which are also found in cavities in the gneiss resembling Alpine clefts.

Hypersthenisation and the chemical transformations in silicate minerals in general are discussed by D. Guimarães.[79]

Olivine from Vesuvius, of very unusual composition, is described by R. Koechlin; [80] the crystals approximate to fayalite in properties and may represent an iron-rich member of the olivine series. An analysis by F. Schwartz of massive white beryl from the S. Tyrol is given by E. Dittler,[81] and the same mineral has been found in Maine in radial aggregates up to 18 feet in length.[82] Euclase from Italy, described by A. Cavinato,[83] resembles that from Brazil; analysis confirms the formula $2SiO_2,Al_2O_3,2BaO,H_2O$.

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[70] "Der Braunstein u. seine Anwendungen" Stuttgart, 1929.

[71] *Amer. J. Sci.*, 1930, [v], **20**, 177.

[72] *Bull. U.S. Geol. Survey*, 1929, **811**, [*D*].

[73] *Tsch. Min. Petr. Mitt.*, 1929, **40**, 191; *A.*, 1930, 57.

[74] *Amer. Min.*, 1930, **15**, 259.

[75] Third Empire Min. Congr., April, 1930.

[76] *Amer. Min.*, 1930, **15**, 65.

[77] *Econ. Geol.*, 1930, **25**, 275.

[78] *Amer. Min.*, 1930, **15**, 280.

[79] *Ann. Acad. Brasil. Sci.*, 1930, **2**, 1; *A.*, 1156.

[80] *Centr. Min.*, 1930, [*A*], 375.

[81] *Tsch. Min. Petr. Mitt.*, 1929, **40**, 188; *A.*, 1930, 57.

[82] E. K. Gedney and H. Berman, *Amer. Min.*, 1930, **15**, 81.

[83] *Atti R. Accad. Lincei*, 1929, [vi], **10**, 656; *A.*, 1930, 448,

Garnet occurs in the Adamello Mountains in reddish-brown dodecahedra, in composition mainly grossularia, and associated with olive-green vesuvianite; analyses and physical constants for both minerals are given by C. Gottfried.[84] An unusual vesuvianite, with 9·20% of BeO, is described by C. Palache and L. H. Bauer.[85] Another garnet, from Avondale, Pa.,[85a] is shown to be a member of the almandite-spessartite series. F. Zambonini and A. Ferrari [86] discuss the crystalline structure and formula of cancrinite; and B. Z. Kolenko [87] describes the distribution of orthite in the Trans-baikal region. Samarskite from New Mexico, analysed by F. L. Hess and R. C. Wells,[88] is believed to have been formed in two generations at different geological periods.

A new silicate from New Zealand, named *ameletite*, is described by P. Marshall: [89] it appears to be a member of the nepheline group and occurs in phonolite in minute crystals and grains that are readily stained by silver nitrate.

Sapphirine from Italy has been analysed by H. P. Cornelius and E. Dittler.[90] Steatite from Bavaria, described by F. Deubel,[91] has been formed by the replacement of quartzite. Highly aluminous altered shales near Postmasburg, S. Africa, contain the interesting minerals diaspore, kaolin, leverrierite, and zunyite; the last is described by L. T. Nel and L. J. Spencer,[92] who discuss the composition in the light of analyses by J. McCrae and H. G. Weall. Gillespite, $FeBaSi_4O_{12}$, occurs with celsian and hedenbergite, for which composition and properties are recorded by W. T. Schaller.[93] *Scawtite*, a new mineral from Co. Antrim described by C. E. Tilley,[94] occurs in vesicles in a hybrid rock formed by the action of a dolerite intrusion upon chalk; it is allied to spurrite, and analysis by M. H. Hey agrees with the formula $6CaO,4SiO_2,3CO_2$.

M. H. Hey [95] has investigated the variation of optical properties with chemical composition in the rhodonite–bustamite series. The minerals are all anorthic, but exhibit variations in the facility of cleavage; density and refractive indices are plotted direct, and it is shown that at 30 mols.% of CaO there is a change in optical sign which is taken as a convenient division between the two minerals forming the series.

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[84] *Chem. Erde*, 1930, **5**, 106. [85] *Amer. Min.*, 1930, **15**, 30; *A.*, 1551.

[85a] *Ibid.*, p. 40. [86] *Atti R. Accad. Lincei*, 1930, [vi], **11**, 782; *A.*, 1397.

[87] *Bull. Acad. Sci. Leningrad*, 1929, 243.

[88] *Amer. J. Sci.*, 1930, [v], **19**, 17; *A.*, 316.

[89] *Min. Mag.*, 1929, **22**, 174; *A.*, 1930, 189.

[90] *Jahrb. Min.*, *Beil.-Bd.*, [*A*], 1929, **59**, 27; *Chem. Zentr.*, 1929, ii, 1640; *A.*, 1930, 316.

[91] *Chem. Erde*, 1930, **5**, 87. [92] *Min. Mag.*, 1930, **22**, 207; *A.*, 570.

[93] *Amer. Min.*, 1929, **14**, 319; *A.*, 1930, 570.

[94] [With M. H. Hey] *Min. Mag.*, 1929, **22**, 222; *A.*, 1930, 569.

[95] *Ibid.*, p. 193; *A.*, 188.

Chabazite has been shown by Y. Tanaka and M. Nakamura [96] to undergo a continuous dehydration on heating up to about 1000° C. It has no adsorptive power even when dehydrated. Heulandite has been studied by P. Gaubert.[97] Crystals occurring at N. Burgess, Ontario, have been identified by R. P. D. Graham and H. V. Ellsworth [98] as cenosite, one of the interesting group of silico-carbonates.

Felspars.—A very detailed examination of the moonstones has been contributed by E. Spencer,[99] who has confirmed the observation that the schiller and microperthitic structures are destroyed by heating to about 1050°. He finds that lamellar albite is selectively attacked by water and carbon dioxide under pressure, which may explain the fact that in some of the natural specimens albite has been completely removed. These results confirm the general view that the peculiar structure of moonstone is due to the separation on cooling of the potash and soda felspars, which are completely miscible in the solid state at high temperatures. Several analyses are given, which lead to certain modifications in the equilibrium diagram for these compounds. The peculiar optical properties of moonstone have also been discussed by A. L. Parsons,[99a] with special reference to the material from Ontario.

Potash felspar apparently exists in dimorphous forms, corresponding with orthoclase (monoclinic) and anorthoclase (anorthic). K. Chudoba [1] has examined the well-known felspar from the trachyte and xenoliths of the Drachenfels and finds that both are anorthic; for this variety he proposes the name *sanidine-anorthoclase.*

The occurrence of potash in the soda–lime felspars is now commonly taken account of, but D. Beliankin [2] points out that other minor constituents cannot be neglected. In a chemical investigation he shows that iron may be present up to 2—3%, whilst barium is often found in the acid felspars : the analyses in certain cases cannot be reconciled with existing theory. Very pure adularia from Japan has been analysed by K. Seto,[3] and H. S. Spence [4] gives analyses of albite and microcline in a description of the pegmatites of Ontario and Quebec, where felspar crystals up to 30 feet in length have been found. F. C. Phillips [5] discusses the pericline twinning of acid plagioclase, and T. F. Barth [6] has described the anorthites from the Adirondacks. Anomalies in the order of zoning of plagioclase have been observed by K. Chudoba.[7]

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[96] *J. Soc. Chem. Ind. Japan*, 1930, **33**, 274.

[97] *Bull. Soc. franç. Min.*, 1929, **52**, 14.

[98] *Amer. Min.*, 1930, **15**, 205.

[99] *Min. Mag.*, 1930, **22**, 291; *A.*, 1397.

[99a] *Amer. Min.*, 1930, **15**, 93.

[1] *Centr. Min.*, 1930, [*A*], 145.

[2] *Bull. Acad. Sci. U.S.S.R.*, 1929, 571; *A.*, 1930, 57.

[3] *J. Petr. Min. Ore Deposits, Japan*, 1929, **1**, 278.

[4] *Amer. Min.*, 1930, **15**, 450.

[5] *Min. Mag.*, 1930, **22**, 225; *A.*, 570.

Clays.—Much work is recorded upon kaolinite and the more acid clays. These minerals, though often minutely crystalline, are not easy to differentiate, but a measure of success has recently been obtained by combining accurate physical determinations with *X*-ray measurements of the crystal structure. C. S. Ross and P. F. Kerr [8] conclude that the kaolin minerals really belong to three distinct species: kaolinite, the chief constituent of china clay; *dickite*, a name now proposed for the mineral first described from Anglesey by A. B. Dick; and nacrite, well known from Freiberg. Kaolinite is much more strongly stained by dyes, but is otherwise very similar to nacrite, while dickite differs in crystal habit and optical properties. All three minerals give distinctive *X*-ray patterns. P. Schachtschabel [9] has studied the dehydration of kaolin; the water is regained under pressure at 200°; the rehydrated mineral, which is at first soluble in hydrochloric acid, gradually approximates in properties to ordinary kaolinite. Kaolin from a metamorphosed ash in N. Carolina is described by J. L. Stuckey; [10] K. Seto [11] gives analyses of material from Korea and Japan; and S. Malkowski and M. Kowalski [12] discuss the occurrence of clays in Poland. Halloysite nodules in limonite from the Harz are described by O. H. Erdmannsdörffer; [13] this mineral loses very little water up to 400°, after which it behaves like kaolin. The more acid clays, usually containing montmorillonite, have considerable commercial importance. They often result from the alteration of volcanic ashes and have the composition $Al_2O_3,3SiO_2$ with a high content of loosely held water. K. Kobayashi and K. Yamamoto [14] describe the Japanese acid clay, which is an altered liparite; the dehydration curve determined by those authors and K. Bitō [15] differs from that of kaolin, while *X*-ray diffraction lines indicate the presence of a distinctive mineral.[16] Bentonite from Arizona, probably formed from volcanic ash that fell into water, is shown by V. T. Allen [17] to consist chiefly of montmorillonite, while E. S. Larsen [18] also describes tuffs from

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[6] *Amer. Min.*, 1930, **15**, 129.

[7] *Centr. Min.*, 1930, [*A*], 145.

[8] *Amer. Min.*, 1930, **15**, 34; *J. Amer. Ceram. Soc.*, 1930, **13**, 151; *A.*, 569.

[9] *Chem. Erde*, 1930, **4**, 395; *A.*, 315.

[10] *Amer. Min.*, 1930, **15**, 10.

[11] *J. Petr. Min. Ore Deposits, Japan*, 1929, **1**, 179; *A.*, 1930, 570.

[12] *Trans. Ceram. Soc.*, 1930, **29**, 142; *A.*, 1397.

[13] *Chem. Erde*, 1930, **5**, 96; *A.*, 732.

[14] *J. Soc. Chem. Ind. Japan*, 1929, **32**, 174; *A.*, 1930, 316.

[15] *Ibid.*, p. 297; *A.*, 316.

[16] N. Kameyama and S. Oka, *ibid.*, 1930, **33**, 29, 92; *A.*, 448, 1017.

[17] *Amer. J. Sci.*, 1930, [v], **19**, 283.

[18] *Bull. U.S. Geol. Survey*, 1929, **811**, [*B*], 89.

Colorado altered to bentonite, and F. Tucan[19] describes a similar silicate having a continuous dehydration curve, from Allchar in Serbia. Nontronite, which has been regarded as ferric kaolinite, appears to belong with the present group, for materials from Bavaria[20] and from Pontevedra[21] both show continuous dehydration at low temperatures and approach the composition $R_2O_3,3SiO_2$. Another member of the group, with 7% of ferrous oxide, near beidellite in composition, is described by I. J. Mickey.[22]

Phosphates.—Near Fairfield, Utah, phosphate nodules from limestone have yielded a remarkable series of minerals described by E. S. Larsen and E. V. Shannon.[23] Wardite,

$$2Na_2O,CaO,6Al_2O_3,4P_2O_5,17H_2O,$$

is shown to be a good species; variscite and pseudowavellite are common. New species are *deltaite*, $8CaO,5Al_2O_3,4P_2O_5,14H_2O$; *dennisonite*, $6CaO,Al_2O_3,2P_2O_5,5H_2O$; *dehrnite*,

$$14CaO,2(Na,K)_2O,4P_2O_5,3H_2O,CO_2,$$

also described from Dehrn with crandallite, $CaO,2Al_2O_3,P_2O_5,6H_2O$; *lewistonite*, $15CaO,(K,Na)_2O,4P_2O_5,8H_2O$; *englishite*,

$$4CaO,K_2O,4Al_2O_3,4P_2O_5,14H_2O;$$

millisite, $2CaO,Na_2O,6Al_2O_3,4P_2O_5,17H_2O$; *lehiite*,

$$5CaO,(Na,K)_2O,4Al_2O_3,4P_2O_5,12H_2O;$$

gordonite, $MgO,Al_2O_3,P_2O_5,9H_2O$. These species are identified by their distinct physical properties, and there are many other substances not yet fully described. Another set of phosphates, described by H. Berman and F. A. Gonyer,[24] occurs in pegmatites at Poland, Maine; amblygonite replaces felspar; analyses are given of lithiophilite, $2(Mn,Fe)O,Li_2O,P_2O_5$; reddingite,

$$3(Mn,Fe)O,P_2O_5,3H_2O;$$

dickinsonite, $7(Mn,Fe)O,2(Na_2,K_2,Ca)O,3P_2O_5,H_2O$; fairfieldite, $(Mn,Fe)O,2CaO,P_2O_5,2H_2O$; *landesite* (new sp.),

$$3Fe_2O_3,20MnO,8P_2O_5,27H_2O.$$

Other phosphates described include lazulite from Chittenden, Vermont;[25] collophane and variscite (Styria).[26] H. R. von Gaertner[27] examines natural and artificial pyrochlore by *X*-rays. The artificial substance is cubic, but natural pyrochlore is " metamict " and only assumes the cubic structure on ignition. The new mineral *bismutotantalite*, Bi_2O_3,Ta_2O_5, is described by E. J. Wayland and

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[19] *Bull. Soc. franç. Min.*, 1929, **52**, 42; *A.*, 1930, 1156.

[20] W. Noll, *Chem. Erde*, 1930, **5**, 373; *A.*, 733.

[21] I. P. Pondal, *Arq. Seminario Est. Galegos*, 1929, **2**, 9; *A.*, 1929, 1418.

[22] *Centr. Min.*, 1930, [*A*], 293.

[23] *Amer. Min.*, 1930, **15**, 303.

[24] *Ibid.*, p. 375.

[25] *Ibid.*, p. 338.

[26] F. Machatschki, *Centr. Min.*, 1929, [*A*], 321.

[27] *Jahrb. Min., Beil.-Bd.*, [*A*], 1930, **61**, 1.

L. J. Spencer.[28] The mineral occurs in a pegmatite in Uganda, in crystals up to several pounds in weight; in composition it corresponds with stibiotantalite.

Seamanite, a new mineral, has the interesting composition $3MnO,(B_2O_3,P_2O_5),3H_2O$; it is described by E. H. Kraus, W. A. Seaman, and C. B. Slawson,[29] from Michigan. It is apparently reddingite with part of the P_2O_5 replaced by B_2O_3.

Carbonates.—J. Romieux[30] has made a detailed study of the distribution of carbonates in the mud of Lake Geneva. Recent algal limestones from S. Australia are described by D. Mawson,[31] and A. L. Mathews[32] concludes that the ooliths of Great Salt Lake form at the water's edge and grow by evaporation of capillary water as they are driven inland by the wind, for they are sometimes zoned with soot. S. Mizgier[33] shows that lublinite is identical with calcite. Structures have been proposed for alstonite and barytocalcite,[34] and analyses are given for gaylussite, nesquehonite, and probertite.

Sulphates, etc.—*Bianchite,* a new white mineral,

$$FeSO_4,2ZnSO_4,18H_2O,$$

is described by C. Andreatta.[35] (Miss) J. M. Sweet[36] gives an account of the occurrence of barytes in Great Britain, and the geology and chemistry of gypsum in New York are discussed by D. H. Newland.[37] Uraninite[38] from Villeneuve, Quebec, yields a variable lead ratio, depending upon the degree of alteration; R. C. Wells[39] gives an analysis of pitchblende occurring with gold in a calcite vein from Chihuahua, Mexico.

Mineral Springs.—Space will not permit detailed reference to the large output of records for mineral springs. American localities include N. Carolina,[40] Arkansas hot springs,[41] and oilfield water in Alberta;[42] data are given for the manganese content of the Mississippi River.[43] Physical constants, etc., for Italian springs are furnished by D. Marotta and C. Sica,[44] R. Nasini and E. Bovalini,[45] and for Sardinia by E. Puxeddu and G. Sanna.[46] At Choussy,[47] France, the medicinal water contains arsenic; tadpoles kept in the well-water showed an increased arsenic content, but this was not so marked when they lived in the bottled water. Other European localities include Upper Checkya (Caucasus),[48] Zagreb [49] district, and Lower Kostrivnica, Jugoslavia.[50] Hydrogen-ion concentration has been determined by M. C. Potter,[51] while O. Baudisch and H. von Euler [52] discuss the phthalein reaction in relation to the state of combination of the iron present. Estimates of the rarer elements have been made spectroscopically on the water of Cambres by A. P. Forjas,[53] and radioactivity determinations by V. Vernadsky [54] (deep springs in Russia) and others. Colorimetric determinations of uranium content on water from Caria, Portugal, are due to H. de Carvalho.[55] O. W. Rees [56] considers that silica in natural-water analyses should be taken into account as an acid radical SiO_3.

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[28] *Min. Mag.*, 1929, **22,** 185; *A.*, 1930, 188.

[29] *Amer. Min.*, 1930, **15,** 220.

[30] *Arch. Sci. phys. nat.*, 1930, **12,** 202; *A.*, 1155.

[31] *Quart. J. Geol. Soc.*, 1929, **85,** 613; *A.*, 1930, 315.

[32] *J. Geol.*, 1930, **38,** 633.

[33] *Z. Krist.*, 1929, **70,** 160; *Chem. Zentr.*, 1929, ii, 544; *A.*, 1930, 188.

[34] *Centr. Min.*, 1930, [*A*], 220, 321.

[35] *Atti R. Accad. Lincei*, 1930, [vi], **11,** 760; *A.*, 1397.

[36] *Min. Mag.*, 1930, **22,** 257; *A.*, 1156.

[37] New York State Mus. Bull., No. 283, 1929.

[38] *Amer. Min.*, 1930, **15,** 455.

[39] *Ibid.*, p. 470.

[40] E. E. Randolph, *J. Elisha Mitchell Sci. Soc.*, 1928, **44,** 70; *A.*, 1930, 187.

[41] *Ind. Eng. Chem.*, 1930, **22,** 632.

[42] *Trans. Canad. Inst. Min. Met.*, 1929, **32,** 316.

[43] *Science*, 1930, **71,** 248.

Distribution of Iodine.—Minute amounts of iodine have been measured in air, dew, in various food-stuffs, and in soils and waters; a survey of the quantity available from these sources at Salta (Argentine) [57] indicates that the average daily intake of iodine per person is below 0·04 mg. and is inadequate. This is primarily due to lack of iodine in food-stuffs, which compare unfavourably with those in non-goitrous districts, even the sheep's thyroid gland showing corresponding deficiency. Iodine surveys are also reported from N. and S. Carolina [58] and Nebraska.[59] Sea-water examined by Winkler's method [60] contains only a small amount of iodine, and the content varies little with the depth. Coal heated with alcohol and potassium carbonate in an autoclave yields a filtrate which can be tested by Winkler's method; twelve mid-European coals show up to 11·17 mg. per kg. By the combustion of coal 7,000,000 kg. of iodine are probably returned to circulation annually.[61] Domestic and drinking waters in E. Prussia sometimes show a high content of iodine.[62]

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[44] *Ann. Chim. Appl.*, 1929, **19**, 529; *A.*, 1930, 448.

[45] *Ibid.*, 1930, **20**, 56, 91; *A.*, 569, 731.

[46] *Giorn. Chim. Ind. Appl.*, 1929, **11**, 438; *A.*, 1930, 187.

[47] *Compt. rend.*, 1930, **190**, 1133. [48] *J. Appl. Chem. Russia*, 1928, **1**, 291.

[49] G. Janeček, *Arhiv Hemiju*, 1929, **3**, 178; *A.*, 1930, 187.

[50] *Bull. Soc. Chim. Roy. Yougoslavie*, 1930, **7**, Reprint.

[51] *Nature*, 1930, **126**, 434; *A.*, 1396.

[52] *Biochem. Z.*, 1929, **212**, 149; *A.*, 1929, 1417.

[53] *Compt. rend.*, 1929, **189**, 703; *A.*, 1929, 1417.

[54] *Ibid.*, 1930, **190**, 1172. [55] *Ibid.*, **191**, 95; *A.*, 1155.

[56] *Ind. Eng. Chem.* (*Anal.*), 1929, **1**, 200; *A.*, 1929, 1417.

[57] P. Mazzocco, *Semana méd.*, 1930, **37**, 358, 364, 366, 370; *A.*, 1015.

[58] J. H. Mitchell, *Science*, 1929, **69**, 650; *A.*, 1929, 1418; J. W. Perry, *J. Elisha Mitchell Sci. Soc.*, 1928, **44**, 87; *A.*, 1930, 187.

[59] W. H. Adolph and F. J. Prochaska, *J. Amer. Med. Assoc.*, 1929, **92**, 2158; *A.*, 1929, 1417.

[60] J. F. Reith, *Rec. trav. chim.*, 1930, **49**, 142; *A.*, 315.

Sea-water.—The composition of the sea near Puget Sound is discussed by T. G. Thompson [63] and others, who give determinations of p_H, chlorine, and dissolved oxygen. In the North Pacific the ionic ratios are constant, namely Ca/Mg 0·3212; Ca/Cl 0·0215; Mg/Cl 0·0669. E. G. Moberg [64] discusses the hydrogen-ion, phosphate, silicate, and fixed nitrogen contents of sea-water. Water from the Red Sea [65] has a very low nitrate content, owing to the predominance of denitrifying bacteria; in consequence, vegetation is scanty. Seasonal variations in phosphate, silicate, and nitrate content in the English Channel [66] are correlated with outbursts of phytoplankton. D. Ellis and J. H. Stoddart [67] describe the chemical effects of sulphur bacteria growing in pools.

Muds.—Considerable attention has been given to the composition of sea and lake muds. H. B. Moore [68] finds that both phosphates and nitrogen diminish with increasing depth in the sea muds of the River Clyde. In Black Sea muds [69] the phosphorus varies inversely with the organic content; vanadium was also determined. In Lake Saki,[70] white deposits of gypsum and sand alternate with black clays which owe their colour to hydrotroilite. The clays react with the salts in solution, and the deposits show seasonal variations. Other factors are the adsorption of salts and the biochemical reduction of sulphates; in the dried mud the latter depends on the sodium chloride content.

The Origin of Coal.—Details of the coal-forming reactions are still keenly debated. A. Duparque [71] suggests that the primordial deposits were of two distinct types, represented by spores, cuticles on the one hand and woody tissue on the other. These have the same chemical composition, and the differences in the coals produced are assigned to secondary changes that vary according to the depth of water, shallow waters yielding anthracites, while the deepest waters yield the boghead coals. H. E. Armstrong [72] concludes that coal is "a condensed material, a natural bakelite." G. Stadnikov [73] discusses in detail the reactions which must have gone to form the Sumpfowy seam, a coal of intermediate character, and suggests that the fats of the algæ from which coorongite has formed must have been reduced by anærobic bacteria in deep salt water, and subsequently oxidised at the surface. Continued anærobic decomposition would yield petroleum. The "lignin theory" has been warmly debated. G. Stadnikov and L. Kaschtanov [74] discuss the chemical character of the compounds that form the Siberian boghead coals; on hydrogenation the cyclic acids eliminate carbon dioxide and are transposed into cyclic hydrocarbons. No phenols are formed.

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[61] E. Wilke-Dörfurt and H. Römersperger, *Z. anorg. Chem.*, 1930, **186**, 159; *A.*, 449.

[62] H. Matthes and G. Wallrabe, *Pharm. Zentr.*, 1930, **71**, 273; *A.*, 886.

[63] *Pub. Puget Sound Biol. Sta.*, 1929, **7**, 65, 119; *A.*, 1930, 731.

[64] Proc. III Pan-Pacific Sci. Cong., 1926, (1928), I, 221; *A.*, 1930, 187.

[65] G. Bini, *Atti R. Accad. Lincei*, 1929, [vi], **9**, 1128.

[66] W. R. G. Atkins, *J. Marine Biol. Assoc.*, 1930, **16**, 821; *A.*, 886.

[67] *J. Roy. Tech. Coll. Glasgow*, 1930, **2**, 336; *A.*, 569.

[68] *J. Marine Biol. Assoc.*, 1930, [ii], **16**, 595; *A.*, 448.

[69] *Bull. Acad. Sci. U.S.S.R.*, 1930, 205.

[70] P. T. Ivanov, *Ann. Inst. Anal. Phys. Chem.*, 1930, **4**, 197; *A.*, 1015.

[71] *Compt. rend.*, 1930, **190**, 1200; *A.*, 887.

Meteorites.—Material from the following localities has been analysed: Sandia Mts.; Hinojo, Buenos Aires; El Mocovi; Cachari; Renca (San Luis); Isthilart; Piedad do Bagre, Minas Geraes. Small amounts of germanium and arsenic have been detected.[75] J. Young has studied the orientation of kamacite,[76] and a general account of the composition and structure has been given by G. P. Merrill.[77] A new iron meteorite from Carbo, Mexico, is described by C. Palache and F. A. Gonyer.[78]

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[72] *Proc. Roy. Soc.*, 1930, [*A*], **127**, 268; *A.*, 887.

[73] *Brennstoff-Chem.*, 1929, **10**, 477; *A.*, 1930, 190.

[74] *Ibid.*, p. 417; *A.*, 57.

[75] J. Papish and Z. M. Hanford, *Science*, 1930, **71**, 269; V. M. Goldschmidt, *Z. physikal. Chem.*, 1930, **146**, 404.

[76] *Min. Mag.*, 1930, **22**, 382; *A.*, 1398.

[77] *Bull. U.S. Nat. Museum*, 1930, No. 149; *A.*, 1157.

[78] *Amer. Min.*, 1930, **15**, 388.

SUB-ATOMIC PHENOMENA AND RADIOACTIVITY.

THE important work of the two years (1929—30) under review has for the most part been physical in character. The new wave-mechanics has been applied to the interpretation of the subject and with increasing success to such processes as the emission of α-particles from the nucleus and the disintegration of the nuclei of the lighter elements by swift α-particles; it is clearly going to play an important part in future work. For the first time new isotopes have been discovered from an examination of band spectra; the new method promises to reveal isotopes at concentrations below those ordinarily detected by the mass-spectrograph. Interesting theories and speculations have been advanced on the nature of the proton, its relation to the electron, and their relative masses, also on the connexion between certain of the fundamental constants of nature. On the chemical side, progress has been made with "the actinium problem," but an important, possibly a deciding datum, the atomic weight of protoactinium, has still to be determined before the outstanding difficulties of the subject are cleared up. The publication at the close of the period of "Radiations from Radioactive Substances" by Lord (formerly Sir E.) Rutherford, J. Chadwick, and C. D. Ellis has given students of radioactivity an admirable summary of the subject on the physical and mathematical sides, and one of unique authority. As the title implies, however, the book covers a narrower range of subjects than earlier works by the senior author; the chemical and geological sides of radioactivity are excellently but only briefly touched upon. A summary of work on β-particles and γ-rays, and other subjects too purely physical in nature to be reported upon here, is given in this book.

Isotopes and Mass-Spectra.

During the period, knowledge of the isotopic constitution of nine elements has been extended. The results are summarised in Table I.

The new isotopes of carbon, nitrogen, and oxygen have been found by detecting and interpreting isotopic lines in band spectra along the lines suggested first by R. S. Mulliken.[1] The first to be found were those of oxygen. Working on data provided for them

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[1] *Ann. Reports*, 1926, **23**, 284.

TABLE I.

Element.	Atomic number.	Minimum number of isotopes.	Masses of isotopes in order of intensities.
Carbon	6	2	12, 13.
Nitrogen	7	2	14, 15.
Oxygen	8	3	16, 18, 17.
Chromium	24	4	52, 53, 50, 54.
Krypton	36	6	84, 86, 82 and 83, 80, 78.
Molybdenum	42	7	98, 96, 95, 92, 94, 100, 97.
Xenon	54	9	129 and 132, 131, 134, 136, 130, 128, 126 and 124.
Tungsten	74	4	184 and 186, 182, 183.
Mercury	80	7	202, 200, 199, 201, 198, 204, 196.

by C. H. Dieke and H. D. Babcock,[2] W. F. Giauque and H. L. Johnston [3] ascribed the weak doublets of the atmospheric absorption bands of oxygen to a molecule $O^{16}O^{18}$. In a later communication,[4] they found other lines which are considered to originate from the molecule $O^{16}O^{17}$. The abundance of these new isotopes is such as not to be detectable by the new mass-spectrograph.[5] The proportion of O^{16} to O^{18} is estimated as 1250 : 1 by H. D. Babcock [6] and also by E. Moles,[7] and as 1075 ± 110 : 1 by S. M. Naudé.[8] That of O^{16} to O^{17} is given as $10^4 : 1$ by W. F. Giauque and H. L. Johnston [4] and also by E. Moles.[7] By a study of the isotope effect in the nitric oxide bands, S. M. Naudé [8] discovered the isotope N^{15}. Band heads were observed in the three bands investigated corresponding with the calculated heads for the molecules $N^{14}O^{16}$, $N^{15}O^{16}$, $N^{14}O^{18}$, and $N^{14}O^{17}$. These indicate the existence of a new isotope N^{15} and confirm O^{17} and O^{18}. The relative abundance of N^{14} to N^{15} was found to be 700 ± 140. This work has been confirmed by G. Herzberg,[9] who investigated the second positive group of nitrogen. His value of the relative abundance is 800 : 1. No evidence of a third isotope N^{16} was found. Carbon also is not a simple element. A. S. King and R. T. Birge [10] found evidence of the existence of the molecule $C^{12}C^{13}$ in the Swan spectrum of neutral C_2, and R. T. Birge [11] of $C^{13}O^{16}$ in absorption spectrograms of CO, and of $C^{13}N^{14}$ in the furnace (emission) spectrogram of CN. Although the evidence is conclusive for the existence of $C^{13}O^{16}$ and

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[2] *Proc. Nat. Acad. Sci.*, 1927, **13**, 670, and unpublished.

[3] *Nature*, 1929, **123**, 318; *A.*, 1929, 369. [4] *Ibid.*, p. 831; *A.*, 1929, 736.

[5] F. W. Aston, *ibid.*, p. 488; *A.*, 1929, 484.

[6] *Ibid.*, p. 761; *A.*, 1929, 624; *Proc. Nat. Acad. Sci.*, 1929, **15**, 471; *A.*, 1929, 971.

[7] *Anal. Fis. Quim.*, 1930, **28**, 127; *A.*, 515.

[8] *Physical Rev.*, 1929, [ii], **34**, 1498; 1930, **35**, 130; **36**, 333; *A.*, 1232.

[9] *Z. physikal. Chem.*, 1930, [*B*], **9**, 43; *A.*, 1084.

[10] *Nature*, 1929, **124**, 127; *A.*, 1929, 970. [11] *Ibid.*, p. 182; *A.*, 1929, 970.

$C^{13}N^{14}$, it is neutral as to that of $C^{12}O^{18}$, and decisive against that of $C^{12}N^{15}$ and $C^{12}N^{16}$. R. T. Birge concluded that C^{13} is more abundant relative to C^{12} than is N^{15} or N^{16} to N^{14}, but no exact data are given.[11a] Although further confirmation and extension of these interesting new results is desired, the results already obtained show that the examination of band spectra afford in certain cases a powerful means of detecting isotopes which are present in relatively small abundance. In the mass-spectrograph very faint lines must necessarily be ascribed to possible impurities, but as each molecule has its own spectrum, impurities in spectra, except in so far as they obscure the lines desired, are immaterial. On the other hand, however, the mass-spectrograph method has the great advantage of giving the absolute masses of isotopes and accurately measuring their relative abundance; the band spectrum method gives only the relative masses of two isotopes and, as recent work [12] has indicated, the intensities of the bands may not be a true measure of the relative abundance of isotopes. One further result has been obtained by this method, *viz.*, the possible existence of Cl^{39}. H. Becker [13] found a third satellite to each absorption line in the hydrogen chloride rotation–vibration spectrum which is satisfactorily explained by the presence of this isotope. This has revived an old suggestion of F. W. Aston which was later rejected by him. Confirmation of the existence of this isotope is highly desirable, for it would make chlorine the first element of odd atomic number to have more than two isotopes and would make 39 the first isobare of odd mass-number to be shared by two elements of odd atomic number.

Continuing his work with the new mass-spectrograph, F. W. Aston has determined the isotopes of chromium,[14] molybdenum,[15] and tungsten,[16] using in each case as source a preparation of the carbonyl. For chromium the mass numbers are 52, 53, 50, and 54 in the relative abundance of 81·6, 10·4, 4·9, and 3·1% respectively. The packing fraction × 10^4 for Cr^{52} is -10 ± 3 ($O^{16} = 0$). The calculated atomic weight derived from these data is 52·011 ± 0·006. For molybdenum the mass numbers are 98, 96, 95, 92, 94, 100, and 97 in the relative abundance of 23·0, 17·8, 15·5, 14·2, 10·0, 9·8, and 9·6% respectively. The packing fractions × 10^4 for Mo^{98} and Mo^{100} are both approximately $-5·5$. The calculated atomic weight is 95·97 ± 0·05. For tungsten the mass numbers are 184,

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[11a] The abundance ratio $C^{13} : C^{12}$ is now given as 1/400 by A. S. King and R. T. Birge; *Astrophys. J.*, 1930, **72**, 19; *A.*, 1931, 15.

[12] A. Elliott, *Nature*, 1930, **126**, 203; *A.*, 1232.

[13] *Z. Physik*, 1930, **59**, 601; *A.*, 393.

[14] *Nature*, 1930, **126**, 200; *A.*, 1232.

[15] *Ibid.*, p. 348; *A.*, 1338.

[16] *Ibid.*, p. 913; *A.*, 1931, 15.

186, 182, and 183 in the relative abundance of 30·1, 30·0, 22·6, and 17·2% respectively. The packing fraction was not accurately measured but is probably zero. The calculated atomic weight is 183·96. In these three cases the atomic weights derived from the data are, it is seen, in excellent agreement with those obtained by chemical means. In another piece of work,[17] however, evidence is adduced by the same author that the accepted atomic weights of krypton and xenon (obtained by physical means) are decidedly lower than those obtained from the data furnished by the mass-spectrograph. He gives details of a method by which the relative abundance of isotopes may be deduced with fair accuracy from the photometry of their lines in mass-spectra, and adds numerical results for the isotopes of krypton, xenon, and mercury. The notion of *isotopic moment* is introduced. This is defined as the sum for all the isotopes of the product of abundance and distance from the mean mass number on the mass scale. This constant is not only roughly proportional to the error to be expected in an atomic weight calculated from mass-spectrum data, but is also an accurate measure of the ease with which the atomic weight may be altered, per unit, in the laboratory by such methods as diffusion or free evaporation. The isotopic moments for krypton, xenon, and mercury are calculated to be 0·87, 1·71, and 1·40 respectively and the corresponding atomic weights are found to be 83·77 ± 0·02, 131·27 ± 0·04 and 200·62 ± 0·05 on the (chemical) scale O = 16. The value for mercury is in good agreement with the accepted value, but each of the others is approximately a unit higher. These discrepancies cannot be ascribed to impurities : suspicion is thrown on the limiting-density method of deriving the values hitherto accepted. In this research, the order of abundance of isotopes of both xenon and mercury has been slightly modified and is that given in Table I. One peculiar and possibly important new feature disclosed is the exact equality in the abundance of certain isotopes of even-numbered elements. Thus Kr^{82} and Kr^{83} are each 11·79% of the whole; Xe^{124} and Xe^{126} are each 0·08%, whilst W^{184} and W^{186}, as the data given above show, are very close in abundance.

Several series of experiments have been carried out to test the unvarying nature of the atomic weights of naturally occuring complex elements. All have given negative results. R. K. McAlpine [18] has failed with antimony, T. W. Richards and A. W. Phillips [19] with copper, G. P. Baxter and S. Ishimaru with nickel,[20] and H. P.

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[17] *Proc. Roy. Soc.*, 1930, [*A*], **126**, 511; *A.*, 393.

[18] *J. Amer. Chem. Soc.*, 1929, **51**, 1745; *A.*, 1929, 971.

[19] *Ibid.*, p. 400; *A.*, 1929, 370.

[20] *Ibid.*, p. 1729; *A.*, 1929, 863.

Cady and H. U. Beecher[21] with nitrogen. At the present time, therefore, boron remains the only element to be different in its isotopic composition according to the part of the world whence it comes.

In the laboratory the work of partially separating isotopes has been continued. F. A. Jenkins[22] has succeeded in obtaining chlorine with so low an atomic weight as 35·418. A. A. Sunier,[23] however, after 13 evaporations of cadium in a vacuum, in each of which half the material was removed, failed to obtain a difference in this constant. The same author[24] discusses critically schemes for fractionating complex elements.

The first forty elements without exception have now been investigated for isotopes. The range of masses is from 1 to 94. The masses still unassigned to any element are in the first decade 2, 3, 5, and 8; in the next two none; in the fourth 38; in the fifth 42, 43, 46, 47, and 49; in the sixth 57; in the seventh 61 and 62; in the eighth and ninth none. Those in the forties may be discovered when F. W. Aston applies to calcium, scandium, titanium, etc., the intensive examination to which chromium, molybdenum, and tungsten have lately been submitted, but the masses 2, 3, 5, and 8 are in different case: 2 and 3 are unlikely ever to be found in hydrogen since they differ relatively so much from the known isotope 1. There is a possibility of 5, however, for helium, and both in band-spectrum work and in an examination of α-particles (in the actinium series) a sharp look-out for this possible isotope might be repaid. 8 is a possibility for beryllium, about which an interesting suggestion has been made by Lord Rayleigh.[25] R. d'E. Atkinson and F. G. Houtermans,[26] in a theoretical investigation of the probability that a proton which has entered a nucleus will anchor itself there by radiating and so build up heavier elements out of lighter, find this possibility much improved if electrons can also penetrate the nucleus. They find that the isotope Be^8 will be one of such products, but will be so unstable as almost certainly to break up into two helium nuclei. This statement has led Lord Rayleigh, who many years ago found that the mineral beryl always contains helium without appreciable quantities of radioactive matter, to suggest that this helium may possibly have arisen from Be^8. If this could be proved, it would indicate that Be^8, even if it does not now exist, has done so within geological times and subsequent to the formation of the mineral.

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[21] *Science*, 1928, **68**, 594; *A.*, 1929, 863.

[22] *Abstr. Theses Univ. Chicago* (*Sci. Ser.*), 1925—26, **4**, 93; *A.*, 1929, 115.

[23] *Ibid.*, p. 173; *A.*, 1929, 115.

[24] *J. Physical Chem.*, 1929, **33**, 577; *A.*, 1929, 666.

[25] *Nature*, 1929, **123**, 607; *A.*, 1929, 487.

[26] *Ibid.*, p. 567; *A.*, 1929, 487.

The discovery of the complexity of oxygen necessitates a reconsideration[27] of the scale on which the weights of atoms are expressed. The present chemical standard is greater than the mass of its main constituent O^{16} by about 1·25 parts per 10^4. This quantity is of little significance to chemists, partly because it is very small and partly because the isotopic constitution of oxygen is probably invariable, but physicists aiming at an accuracy in the masses of atoms of 1 part in 10^5 parts must find the chemical unit unsuitable. The masses of the proton, the neutral hydrogen atom, one-quarter of the neutral helium atom, one-sixteenth of the neutral oxygen atom, O^{16}, have been the chief suggestions for the standard mass. It should be pointed out that apart from this difference in the scale, the atomic weights of nitrogen and carbon cannot now be the same as the masses N^{14} and C^{12} respectively determined by the mass-spectrograph. Calculated values of these are given by S. M. Naudé.[8]

Radioactive Constants and Other Data.

A new value of the half-period of ionium, $1{\cdot}9 \times 10^5 \pm 3\%$ years, has been obtained by (Mme.) P. Curie and (Mme.) S. Cotelle[28]; this is considerably higher than early values. Two values for the half-period of radium-*D* are also considerably higher than earlier values. (Mme.) P. Curie and (Mme.) I. Curie[29] obtained 19·5 years by direct measurements over a period of 16 years, and the latter[30] obtained 23 years by an indirect method. The value 21 years is provisionally adopted. F. Joliot,[31] by a slight modification of J. C. Jacobsen's[32] method, obtained the half-period of radium-*C′* as $3 \pm 1{\cdot}5 \times 10\ ^{6}$ sec., confirming the order of the period previously obtained. A similar experiment with thorium-*C′* showed that its period is much less than 10^{-6} sec. The half-periods of potassium and rubidium have been determined by W. Mühlhoff[33] by counting the number of β-particles emitted per g. per sec. in a Geiger and Müller sensitive particle counter. The half-period for potassium is $1{\cdot}5 \times 10^{13}$ years, which is ten times greater than that estimated by A. Holmes and R. W. Lawson[34]; that of rubidium is $4{\cdot}3 \times 10^{11}$

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[27] F. W. Aston, *Nature*, 1930, **126**, 953; A. von Grosse, *Z. physikal. Chem.*, 1930, [*B*], **10**, 395; *A.*, 1931, 15.

[28] *Compt. rend.*, 1930, **190**, 1289; *A.*, 976.

[29] *J. Phys. Radium*, 1929, [vi], **10**, 385; *A.*, 8.

[30] *Ibid.*, p. 388; *A.*, 8.

[31] *Compt. rend.*, 1930, **191**, 132; *A.*, 1086.

[32] *Phil. Mag.*, 1924, [vi], **47**, 23; *A.*, 1924, ii, 142.

[33] *Ann. Physik*, 1930, [v], **7**, 205; *A.*, 1496.

[34] *An n. Reports*, 1928, **25**, 308.

years. On the assumption that the radioactivity of potassium is due only to K^{41}, the half-period of this isotope becomes 10^{12} years, since K^{41} is approx. 6·7% of the total potassium (and not 5% as is generally assumed from the atomic-weight determination in ignorance of the exact masses of K^{39} and K^{41}). The new result for potassium is important in connexion with J. Joly's theory of the surface history of the earth, and has been briefly discussed by him.[35]

Attempts to accelerate or influence the rate of decay of a radioactive substance by bombarding it with α-particles have never been substantiated. H. Herszfinkiel and L. Wertenstein [36] have pointed out that this unexpected apparent stability may be due to the fact that the experimenter may have been looking for a product which is in fact not produced. For example, the bombardment of uranium-I has been expected to produce the quick-changing uranium-X_1 due to loss of an α-particle, whereas on Lord Rutherford's theory [36a] it might instead produce uranium-II by loss of an α-particle and two β-particles; since uranium-II is a product of long half-period the possible effect of the bombardment might have gone undetected. With thorium, however, the transformation would produce the relatively quick-changing radiothorium, which would be much more easily detected. A milligram of thorium oxide was bombarded by the α-particles from 28 millicuries of radon for 6 days. No change of activity could be detected by a method which was sensitive to 0·05 mg. of thorium. It was concluded that, if bombardment produced radiothorium from thorium, not more than one α-particle in 8 × 10^6 could have been effective. G. I. Pokrowski,[37] however, found with weak sources of active material that the probability law for the number of particles expelled was regularly deviated from, and concludes that the disintegration of one atom is not independent of that of its neighbours. (Mme.) P. Curie [38] has given an account of experiments undertaken under her direction to influence the values of the disintegration constants, and concludes that this cannot be done. She criticises [39] adversely the work of L. B. Bogoiavlenski,[40] who claims that polonium disintegrates at different rates in different parts of Russia, the rate of decay being least abnormal in the capital.

The round value for the constant Q, the number of α-particles emitted per g. of radium (without products) per sec. must now be accepted as $3{\cdot}70 \times 10^{10}$. By means of the " total charge " method, H. J. J. Braddick and H. M. Cave[41] obtained the value $3{\cdot}68 \times 10^{10} \pm 1\%$. With a new type of electrical counter due to H. Greinacher,[42] F. A. B. Ward, C. E. Wynn-Williams, and H. M. Cave[43] obtained the value $3{\cdot}66 \times 10^{10} \pm 0{\cdot}5\%$. In both these sets of experiments the source employed was radium-*C*, and the value of the standard used was assumed to be accurately known. In the new electrical counter, the ionisation produced by a single α-particle is linearly amplified by triode valves, there being no ionisation by collision. The final deflexion of the recording instrument is proportional to the initial ionisation. The ionisation due to β-particles is too small to disturb the counting, which can be carried out accurately at so high a rate as 500 particles per minute. This value confirms that of V. F. Hess and R. W. Lawson[44] which has been opposed for many years to that of H. Geiger and A. Werner[45]. The $3{\cdot}7 \times 10^{10}$ value has now been got by the electric counting, the total charge, the production of helium,[46] the volume of radon,[47] and the heating-effect methods.[48] The half-period of radium calculated from this datum is 1600 years.

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[35] *Nature*, 1930, **126**, 953.

[36] *Ibid.*, 1928, **122**, 504; *A.*, 1928, 1169.

[36a] See ref. 79.

[37] *Z. Physik*, 1929, **58**, 706; 1930, **65**, 133; *A.*, 1930, 9, 1496.

[38] *J. Phys. Radium*, 1929, [vi], **10**, 329; *A.*, 1929, 1358.

[39] *Ibid.*, p. 327; *A.*, 1929, 1358.

[40] *Ibid.*, p. 321; *A.*, 1929, 1358; *Nature*, 1929, **123**, 872; *A.*, 1929, 737.

G. I. Harper and E. Salaman[49] found the range of polonium α-particles to be 3·87 cm. in standard air (15° C. and 760 mm.). J. L. Nickerson[50] found that of thorium α-particles to be $2{\cdot}75 \pm 0{\cdot}1$ cm. The former is about 0·05 cm. less than the generally accepted value, but is in agreement with an earlier determination of (Mlle.) I. Curie[51]; the latter value is 0·15 cm. less than the accepted value. The first authors also found that the ranges of thorium-*C''*, radium-*C'*, and thorium-*C* are all smaller than has previously been recorded. The deviation is greatest for thorium-*C*, and appears to be definitely outside of the range of experimental error.

Important work on the initial velocities of the α-particles from radium-*C'*, thorium-*C'*, and actinium-*C* has been done. G. C.

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[41] *Proc. Roy. Soc.*, 1928, [*A*], **121,** 367; *A.*, 1929, 6.

[42] *Z. Physik*, 1926, **36,** 364; *A.*, 1926, 553; *ibid.*, 1927, **44,** 319; *A.*, 1927, 915.

[43] *Proc. Roy. Soc.*, 1929, [*A*], **125,** 713; *A*, 7.

[44] *Sitzungsber. K. Akad. Wiss. Wien*, 1918, [2*A*], **127,** 405.

[45] *Z. Physik*, 1924, **21,** 187; *A.*, 1924, ii, 226.

[46] (Sir) J. Dewar, *Proc. Roy. Soc.*, 1910, [*A*], **83,** 404; *A.*, 1910, ii, 376.

[47] L. Wertenstein, *Phil. Mag.*, 1928, [vii], **6,** 17; *A.*, 1928, 932.

[48] E. Rutherford and H. Robinson, *ibid.*, 1913, [vi], **25,** 312; *A.*, 1914, ii, 789; S. W. Watson, *Proc. Roy. Soc.*, 1928, [*A*], **118,** 318; *A.*, 1928, 455.

[49] *Proc. Roy. Soc.*, 1930, [*A*], **127,** 175; *A.*, 659.

[50] *Trans. Nova Scotia Inst. Sci.*, 1930, **17,** 172; *A.*, 659.

[51] *Ann. Reports*, 1926, **23,** 291.

Laurence,[52] continuing the work of G. H. Briggs,[53] has found the initial velocities of the α-particles from radium-*C*, thorium-*C*′, and polonium to be 1·709, 2·054, and 1·592 × 10^9 cm. per sec., respectively, assuming Briggs's value for radium-*C*′, *viz.*, 1·923 × 10^9 cm. per sec. S. Rosenblum,[54] using a magnetic deviation method, found the initial velocities of the α-particles from radium-*C*′, thorium-*C*′, and radium-*A* to be 1·923, 2·054, and 1·695 × 10^9 cm. per sec. respectively, assuming Briggs's value for thorium-*C*, *viz.*, 1·701 × 10^9 cm. per sec. The three sets of values are in excellent agreement. S. Rosenblum [55] has also made the remarkable observation that the initial velocity of the ordinary α-particles from some radio-elements is not a constant. He examined the fine structure of the α-particles from thorium-*C* (range 4·8 cm.) by the Danysz focusing method employed in the examination of β-particle spectra. The particles were bent in a circle of about 25 cm. diameter by means of a field of about 36,000 gauss. He found that four faint groups accompany the main group of particles. Their velocities were 1·003, 0·975, 0·962, and 0·964, that of the main group being 1, and their relative intensities were 30, 3, 2, and 0·5% respectively of that of the main group. He obtained no certain evidence of additional groups of particles from radium-*A*, polonium, radium-*C*′, or thorium-*C*′. This new method of attack is clearly one of interest and importance. Another method of analysis of groups of α-particles has been devised by Lord Rutherford, F. A. B. Ward, and C. E. Wynn-Williams.[56] By using a double ionisation chamber with a Greinacher counter,[42] they have succeeded in counting, not simply the total number of particles exceeding a given range, but the number having ranges between *x* and *x* + *dx*, where *dx* is a few millimetres only. With this apparatus they have investigated the straggling curves of the 8·6-cm. α-particles from thorium-*C*′, the 7·0-cm. particles from radium-*C*′, and the 3·9-cm. particles from polonium. All these, in confirmation of S. Rosenblum's results, appear to be homogeneous groups of α-particles. They have shown also that the 5·5-cm. particles from actinium-*C* are in two well-marked groups of ranges 5·51 and 5·09 cm. in the ratio of 100 : 22. They found for the first time the short-range α-particles postulated by the group-displacement law and the Geiger–Nuttall relation, emitted in the dual disintegration of radium-*C*. There are two sets with ranges of 4·14 and 3·95 cm., assuming the range of the α-particles of polonium to be 3·92 cm. Their relative intensities are 3 to 1. The intensity of the two groups together is just over 1 in 4000 of the main 7-cm. group of particles from radium-*C*′. The branching at radium must now be taken as 4000 to 1 in the directions radium-*C*′ and radium-*C*″ respectively, a value in good agreement with those deduced by K. Fajans [57] (3000 : 1), and by (Frl.) E. Albrecht [58] (4000 : 1), from the intensity of the β-particles from radium-*C*. The experimental values of the ranges are in agreement with that deduced from the Geiger–Nuttall relation (3·9 cm.). Finally, the 4·8-cm. α-particles from thorium-*C* were found to be complex, in qualitative agreement with S. Rosenblum's work. It is probably significant that those products, radium-*C*, thorium-*C*, and actinium-*C*, which give complex α-particles, are all of odd atomic number, and it will be interesting to see whether protoactinium, when it is examined, conforms to this. This heterogeneity is not explained by earlier theories of the structure of radioactive nuclei, but an explanation of it has since been put forward by G. Gamow.[59]

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[52] *Proc. Roy. Soc.*, 1929, [*A*], **122**, 543; *A.*, 1929, 370.
[53] *Ibid.*, 1928, [*A*], **118**, 549; *A.*, 1928, 569.
[54] *Compt. rend.*, 1930, **190**, 1124; *A.*, 837.
[55] *Ibid.*, 1929, **188**, 1401, 1549; *A.*, 738; *ibid.*, 1930, **190**, 19.
[56] *Proc. Roy. Soc.*, 1930, [*A*], **129**, 211; *A.*, 1338.

New data have been obtained of the relative abundance and ranges of the long-range particles from radium-*C*′ and thorium-*C*′. Using a special form of Wilson expansion apparatus, R. R. Nimmo and N. Feather [60] find that the long-range particles of thorium-*C*′ fall into two principal groups of ranges 9·82 and 11·62 cm. in standard air, the range of the ordinary α-particle being taken as 8·54 cm. The ratio of the abundance 1 : 5·1 differs considerably from that obtained by (Frl.) L. Meitner and K. Freitag [61] (1 : 2·8). A few tracks indicating α-particles of range 12·5 cm. were observed, but the number was too small to allow definite conclusions to be drawn. The conclusions for radium-*C*′ were less definite. There is a well-defined group with a range of 9·08 cm., but other particles have ranges fairly well distributed between 7·5 and 12 cm. These may be regarded as groups with mean ranges of 8·0, 11·0, and possibly also 10·0 cm. The results, however, make it quite clear that radium-*C*′ emits more than the two long ranges found in the original scintillation experiments of Rutherford and J. Chadwick.[62] On the other hand, K. Philipp and K. Donat,[63] using also Wilson's cloud method, find that for every 10^6 normal α-particles from radium-*C*′ there are 29 with a range of 9·2 cm., 4 of 11·0 cm.,

[57] *Physikal. Z.*, 1912, **13**, 699; *A.*, 1912, ii, 824.

[58] *Sitzungsber. K. Akad. Wiss. Wien*, 1919, [2 *A*], **128**, 925; *A.*, 1921, ii, 675.

[59] *Nature*, 1930, **126**, 397; *A.*, 1339.

[60] *Proc. Roy. Soc.*, 1929, [*A*], **122**, 668; *A.*, 1929, 371.

[61] *Z. Physik*, 1926, **37**, 481; *A.*, 1926, 772.

[62] *Phil. Mag.*, 1924, [vi], **48**, 509; *A.*, 1924, ii, 814.

[63] *Z. Physik*, 1929, **52**, 759; *A.*, 1929, 371.

and 0·5 with a range greater still. These data confirm the scintillation experiments. The origin of the long-range particles is discussed by Rutherford, J. Chadwick, and C. D. Ellis and, for thorium-*C*′, by E. Stahel.[64]

H. Zeigert[65] has determined the number of ions produced per α-particle from uranium-I, uranium-II, and radium by detecting single α-particles with a very sensitive electrometer and measuring directly the total ionisation in air due to each. The values $1{\cdot}16 \times 10^5$, $1{\cdot}29 \times 10^5$, and $1{\cdot}36 \times 10^5$ are in good accord with the values calculated from the ranges of these elements based on the range of radium-*C*′ and the number of ions it produces.

The Actinium Problem.

In a mass-spectrograph investigation of uranium-lead tetramethyl prepared from bröggerite, F. W. Aston[66] found the isotopes Pb^{206}, Pb^{207}, and Pb^{208} in the abundance of 86·8, 9·3, and 3·9% respectively. Pb^{207} in this proportion cannot be due to ordinary lead, and it is concluded that it is the end product of the actinium series. This experiment brilliantly establishes a suggestion, many years old, based partly on atomic-weight determinations and partly on the half-periods of disintegration products. Calculated from this result, the atomic weight of protoactinium becomes 231 or, if allowance is made for the packing effect by extrapolating the packing-fraction curve, 231·08. On the basis of this work, Rutherford[67] supposes that an isotope of uranium-I, actino-uranium, of mass 235, is the head of the actinium series proceeding to protoactinium *via* uranium-*Y*. From the half-value period of uranium-I, he calculates the period of actino-uranium to be $4{\cdot}2 \times 10^8$ years, and deduces that, if the production of uranium in the earth ceased as soon as the earth separated from the sun (as is likely), the earth cannot be older than $3{\cdot}4 \times 10^9$ years. Also if the age of the sun be taken as about 7×10^{12} years (Sir J. Jeans's estimate), it follows that uranium and similar elements were being formed in the sun as late as 4×10^9 years ago and that probably the process still continues. Although there is agreement that the atomic weight of actinium-Ω must be accepted as 207, the other points raised have received criticism. C. N. Fenner and C. S. Piggot,[68] from a study of the composition and age of the bröggerite from which the lead was obtained, regard Aston's determination of the abundance of Pb^{208} as about 50% too high, since, on his figures, the uranium–thorium equivalence factor (0·38) comes out at 0·57. By inference, the abundance of Pb^{207} is also 50% too high. A. Holmes [69] has directed attention to another line of evidence, from which it can be inferred that the half-periods of uranium-I and actino-uranium are probably nearly equal. It has been generally accepted that the percentages of atoms disintegrating *via* protoactinium and radium from uranium are about 3 and 97 respectively. If both uranium-I and actino-uranium disintegrate at about equal rates, these should be the percentages of Pb^{207} and Pb^{206} in pre-Cambrian minerals. But if Rutherford is right, the percentage of Pb^{207} should be definitely higher. From composition and atomic-weight data of four unaltered minerals, Holmes calculates the percentage of Pb^{207} to be between 2·5 and 3·3. He concludes that Aston's estimate of the abundance of Pb^{207} in bröggerite is too high to be representative, that Rutherford's resulting estimate for the half-period of actino-uranium is too low, and that, indeed, the half-periods of uranium-I and actino-uranium are probably of the same order. This agreement in the proportion of corresponding actinium and uranium members at the beginning and at the end of their series is remarkable, but it does not include all the evidence. There are atomic-weight determinations of uranium-lead which suggest that Pb^{207} is totally absent from it [69, 70]. Again, J. E. Wildish [71] found that the number of atoms of protoactinium disintegrating per 100 atoms of uranium varied from 1·47 to 5·16 in different minerals. The lower values could, no doubt, be explained by alteration of the mineral, but not the upper. It is difficult to see also how F. W. Aston's result for Pb^{207} could be cut down to 3 or even 5%. Also, A. F. Kovarik,[72] from a survey of evidence not dissimilar from that considered by A. Holmes, considers that actino-uranium has a half-period of $2·7 \times 10^8$ years, a value even lower than Rutherford's. Initially, he thinks, there has been a definite amount in proportion to the uranium-I, but the relative proportion of the two isotopes has decreased with the age of the mineral. The period of actino-uranium cannot, therefore, be regarded as settled so long as this conflict of evidence and opinion remains. The mass of this isotope must meanwhile be taken as 235, as suggested by Lord Rutherford. The determination of the atomic weight of protoactinium (the result of which has not yet been published) or of the constitution of uranium by the mass-spectrograph method should settle this point. But, as it has not been settled, it may be said that it is exceptional that ordinary uranium should have an isotope of odd mass like 235, possibly in so great an abundance (by weight) as 3% (on A. Holmes's evidence) when it apparently contains no mass of 236 or 240, and when the abundance of uranium-II, of mass 234, is negligible. A. S. Russell [73] has previously given reasons for regarding 233 as a more likely mass for protoactinium than 231. This appeared to require a mass for actinium-Ω of 209 which is certainly wrong, but only if no other massive particle than the α-particle is expelled in the series. From general knowledge of the masses and stabilities of isotopes both of radioactive and inactive elements, it seems simplest to regard actino-uranium as having a mass of 238, protoactinium one of 233, and actinium-Ω one of 207. An experimental value of protoactinium of 233 would support this view with its consequence that the α-particle is not the only massive particle expelled; a value of 231 would favour the much simpler view.

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[64] "Radiations from Radioactive Substances," p. 94; E. Stahel, *Z. Physik*, 1930, **63**, 149; *A.*, 1233.

[65] *Z. Physik*, 1928, **46**, 668; *A.*, 1928, 455.

[66] *Nature*, 1929, **123**, 313; *A.*, 1929, 370.

[67] *Ibid.*, p. 313; *A.*, 1929, 373.

[68] *Ibid.*, p. 793; *A.*, 1929, 620.

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[69] *Nature*, 1930, **126**, 348; *A.*, 1339. [70] *Ann. Reports*, 1928, **25**, 306.

[71] *J. Amer. Chem. Soc.*, 1930, **52**, 163; *A.*, 308.

[72] *Science*, 1930, **72**, 122; *A.*, 1495; *Amer. J. Sci.*, 1930, [v], **20**, 393; *A.*, 1552.

The actinium problem is also discussed by G. Elsen,[74] A. von Grosse,[75] and T. R. Wilkins.[76] The first author supports a view, now out of favour, that the atomic weight of actino-uranium is greater than 238; and the last worker is in agreement with Lord Rutherford in regarding its period as less than that of uranium-I.

Wave-mechanics and Radioactive Disintegration.

A simple explanation of radioactive disintegration and a solution of the apparent conflict between the radioactive data and the results of scattering has been put forward simultaneously by G. Gamow [77] and by R. W. Gurney and E. U. Condon [78] on a basis of the new wave-mechanics. It deals with the points such as the exponential law of transformation and the Geiger–Nuttall relation which were left untouched by Rutherford's theory [79] of the structure of radioactive nuclei. The nucleus is pictured as a tiny enclosure surrounded by a potential hill enclosing an α-particle (represented by a standing wave) of which the energy is less than the potential energy at the top of the barrier. On the classical mechanics, the α-particle inside the nucleus cannot surmount the barrier, but, on wave mechanics, it will have a finite chance of escape which will be the greater the greater its energy, the thinner the barrier, and the smaller the height of the barrier (see these Reports, p. 27). There is thus a relation between the energy of the α-particle and the disintegration constant of the nucleus. Gamow expresses this as $\log \lambda = k + bE$, where λ is the disintegration constant, k a constant, b a constant for all radioactive nuclei, and E the energy of the α-particle. This corresponds approximately to the Geiger–Nuttall relation, and the calculated value of b corresponds well with the experimental value. Log λ, it is seen, increases less rapidly than E, a relation which is consistent with the fact that the half-period of a quick-changing product like radium-C' is much less than is anticipated from the Geiger–Nuttall relation. The theory has been developed by G. Gamow and F. G. Houtermans.[80] They show how the disintegration constants of all α-particle elements can be calculated from the nuclear charge and the velocity of the α-particle. The calculated values are in very satisfactory agreement with the experimental, in view of the approximations made in the calculations. The theory, though still in a tentative form, is most promising. It may be added that it demands such potential barriers round radioactive nuclei as not to be penetrated by any α-particles at present available, and this is in agreement with experimental work.

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[73] *Nature*, 1927, **120**, 402; *A.*, 1927, 1002.

[74] *Z. anorg. Chem.*, 1929, **180**, 304; *A.*, 1929, 737.

[75] *Ibid.*, 1930, **186**, 38; *A.*, 515.

[76] *Physical Rev.*, 1927, [ii], **29**, 352; *A.*, 1928, 1302.

[77] *Z. Physik*, 1928, **51**, 204; *A.*, 1929, 7; *ibid.*, 1929, **53**, 601; *A.*, 1929, 484.

[78] *Nature*, 1928, **122**, 439; *Physical Rev.*, 1929, [ii], **33**, 127; *A.*, 1929, 374.

[79] *Phil. Mag.*, 1927, [vi], **4**, 580; *A.*, 1927, 1002; *Ann. Reports*, 1928, **25**, 309.

Artificial Disintegration by α-Particles.

The divergences[81] between the two series of investigations on the artificial disintegration of the light elements carried out at Cambridge and at Vienna have still to be satisfactorily explained. As these relate to the detection of scintillations, it is obvious that some of the doubtful points would be cleared up by obtaining photographs of the disintegration in a Wilson cloud chamber or by using an electrical method of detecting the particles of disintegration. First steps in both these directions have already been taken and, it is hoped, will lead ultimately to a solution of the difficulty.

While a general description of the phenomena of disintegration can be given in terms of the picture of the potential field between an α-particle and the nucleus of a light atom obtained from the scattering experiments, there are still a few outstanding difficulties. The data suggest that penetration of the α-particle into the aluminium nucleus and capture, for instance, would be impossible for velocities of α-particles less than 2×10^9 cm. per sec., while actually the aluminium nucleus is disintegrated by particles of much smaller velocity. An explanation of this, impossible on classical mechanics, is given by G. Gamow [77] and by R. W. Gurney and E. U. Condon [78] on the basis of wave-mechanics. The agreement between Gamow's calculations of the chance of penetration and the experimental numbers of emitted protons is sufficient to show that, for elements like nitrogen or aluminium, the probability that a capture of the α-particle results in disintegration is fairly high. Gamow [82] has also calculated the probability of disintegration of light elements when bombarded by α-particles from radium-C' and from polonium, and shown that the chance of penetration decreases very rapidly as atomic number increases and is small for numbers greater than 20. The possibility, therefore, that eventually all elements will be brought into line with the lighter ones in this respect is exceedingly remote.

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[80] *Z. Physik*, 1928, **52**, 496; *A.*, 1929, 233.

[81] *Ann. Reports*, 1926, **23**, 285.

The bombardment of atoms of aluminium by α-particles of range 7 cm. from radium-$(B + C)$ has been shown by Rutherford and J. Chadwick [83] to release protons with a definite minimum range in air of about 10—12 cm. These experiments suggest that the protons liberated in disintegration possess a certain minimum energy in addition (as had been shown earlier) to a maximum energy. This energy of release for aluminium is roughly of the same magnitude as that corresponding with the potential of a proton in the field round the aluminium nucleus.

F. W. Aston's [84] observation that the packing fraction is higher for light elements of odd atomic number than for those of even, is correlated [85] with the observation that protons emitted from elements of odd atomic number have greater maximum energies in general than those emitted from elements of even atomic number. For if the disintegration consists of the capture of an α-particle and the emission of a proton, the odd-numbered element bombarded is changed to an even-numbered element and *vice versa*. In the former case mass is lost, in the latter mass is gained. The loss will appear as an excess of kinetic energy associated with the emitted proton above that which can exist in the latter case. In this argument, the gain in mass of the proton on its release from the nuclear binding and the kinetic energy of the incident α-particle have not been taken into account. These energies, however, nearly balance; the gain in mass in the former case, 0·00724, being close to the mass equivalent of the kinetic energy of the α-particle (of radium-C'), *viz.*, 0·0082. But the information at present available is not sufficiently accurate to test this point more than qualitatively. For quantitative agreement, the atomic masses of the lighter elements must be known with a greater degree of accuracy than at present, and the motions of the α-particle and the residual nucleus after disintegration must also be accurately known. At present the available evidence is against quantitative agreement.[86]

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[82] *Nature*, 1928, **122**, 805; *A.*, 1929, 6; *Z. Physik*, 1928, **52**, 510.

[83] *Proc. Camb. Phil. Soc.*, 1929, **25**, 186.

[84] *Ann. Reports*, 1928, **25**, 303.

[85] J. Chadwick, *Proc. Roy. Soc.*, 1929, [*A*], **123**, 373; *A.*, 1929, 622.

The new wave-mechanics has also been applied to explain artificial disintegration by α-particles.[87] It has been suggested by J. Chadwick and G. Gamow,[88] partly on general grounds and partly on the basis of unpublished experiments at Cambridge, that the process of disintegration of a nucleus by collision with an α-particle may occur in two ways : (*a*) by the capture of the α-particle by the atomic nucleus followed by the emission of a proton, and (*b*) (a new suggestion) by the ejection of a proton without the capture of the α-particle. In (*a*) the α-particle must penetrate the nucleus; in (*b*) it need not, collisions being responsible for the disintegration. It is deduced that there may be more than one level at which the α-particle may remain after capture and that there will be protons of "the line spectrum" and protons of "the continuous spectrum." The former are expected to be emitted nearly uniformly in all directions, the latter will be emitted mainly in the direction of the colliding α-particles. Experimental evidence for the presence of groups of different ranges in the disintegration protons has already been obtained by different experimenters.[89] When boron, for example, is bombarded by the α-particles of polonium, three groups of protons have been found with ranges in air of 16, 32, and 76 cm. The first is identified as a "continuous spectrum," and the other two as "line spectra." From energy considerations it appears that B^{10} is the isotope attacked. The continuous spectrum of protons is interpreted as corresponding with the formation of the nucleus of Be^9 and both the line groups with that of C^{13}. The disintegration of aluminium by the α-particles from polonium shows similar features. Although such experimental results are still at a tentative stage, it is evident that the phenomenon of artificial disintegration promises to reveal the intimate structure of the nuclei of the lighter elements in a way not previously thought possible.

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[86] "Radiations from Radioactive Substances," p. 307.

[87] *Ibid.*, p. 572.

[88] *Nature*, 1930, **126**, 54; *A.*, 1085.

[89] W. Bothe and H. Fränz, *Naturwiss.*, 1928, **16**, 204; *A.*, 1928, 1302; *Z. Physik*, 1928, **49**, 1; **51**, 613; *A.*, 1929, 230; H. Fränz, *ibid.*, 1930, **63**, 370; *A.*, 1338; *Physikal. Z.*, 1929, **30**, 810; *A.*, 130; W. Bothe, *Z. Physik*, 1928, **51**, 613; *A.*, 1929, 230; *ibid.*, 1930, **63**, 381; *A.*, 1339; H. Pose, *ibid.*, **64**, 1; *A.*,1232; *Physikal. Z.*, 1929, **30**, 780.

It is interesting to note that the two synthesised nuclei, O^{17} and C^{13}, have been discovered from an examination of band spectra.[90]

The Scattering of α-Particles in Helium.

An interesting contribution to this subject has been made by J. Chadwick.[91] The problem of the collision of two particles which act upon each other with forces varying as the inverse square of the distance between them has been solved exactly on the basis of the new wave-mechanics, and the solution is the same as that given by the classical mechanics. This agreement, however, as N. F. Mott[92] has pointed out, depends upon the dissimilarity of the colliding particles; if the particles are identical, the scattering laws given by the wave-mechanics will be very different from those of classical theory. α-Particles from polonium were scattered through angles between 40° and 50°. The experimental results were found to be close to those predicted by the quantum theory and markedly different from those predicted on the classical theory. The calculations of Mott are therefore verified, and with them the assumption on which they rest, *viz.*, that it is impossible to distinguish one helium nucleus from another. In other words, the helium nucleus has no spin or vector quantity associated with it. Its field of force is perfectly spherical. The observations also indicate that, as the distance between the colliding α-particle and nucleus is decreased, the observed scattering rises slightly above that calculated from the quantum theory, then falls, and finally rises rapidly again. The initial rise and fall may be due to a true change in the law of force between the particles, but the asymmetry shown at small distances of collision can be due only to a distortion of the structure of the particles.

The Age of Iron Meteorites.

F. Paneth, W. D. Urry, and W. Koeck[93] have determined the age of 27 different specimens of iron meteorites by ascertaining the ratio of helium to uranium. The helium was estimated by Paneth's improved method, and the uranium by a radium determination. The ages calculated from the experimental data are all less than the age of the earth, and the results agree with the view that the meteorites originated in the solar system. Earlier determinations of age by the helium method were shown to be too low owing to the incomplete evolution of the gas by the methods employed.

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[90] *Supra*, p. 306.

[91] *Proc. Roy. Soc.*, 1930, [*A*], **128**, 114; *A.*, 1085.

[92] *Ibid.*, **126**, 259; *A.*, 269.

[93] *Nature*, 1930, **125**, 490; *A.*, 571; *Z. Elektrochem.*, 1930, **36**, 727; *A.*, 1398.

The Cosmic Rays.

Hitherto the penetrating radiation usually known as the cosmic rays has been regarded as electromagnetic in character and coming from outer space.[94] W. Bothe and W. Kolhörster,[95] however, have done experiments which suggest that it is corpuscular. They arranged two Geiger counters of special design a small distance apart inside a protecting shield of iron and detected the same β-particle inside each. They concluded from their experiments that the primary penetrating radiations are very high-speed β-particles. The number of these is very small, about 1/100 per sq. cm. per sec., but their individual energies must be very high. E. Regener,[96] on the other hand, has measured the absorption coefficient of the radiation in water to such great depths that it is seems very unlikely it could be corpuscular in character. He made measurements at distances from 32 to 231 metres, obtaining seven readings, below the level of Lake Constance. The maximum distance he attained to is about three times greater than the region explored by R. A. Millikan and G. H. Cameron.[94] A single absorption coefficient of value about 0·018 per metre of water was found to explain the absorption at depths greater than 80 metres, a value which implies a penetrating power greater than any of those found by Millikan and Cameron. A. Corlin [97] has made a critical examination of the systematic measurements to determine whether the penetrating radiation is in any way directional. He concludes that the intensity of it is periodic. It is relatively high at 3 p.m. and possibly between 5 and 8 a.m. and low at 10 a.m. As V. F. Hess and O. Mathias [98] did not find such periodic fluctuations with their electroscope covered with 7 cm. of iron, it was concluded that only the softer components follow sidereal time. Fluctuations, however, have been also found by E. Regener [96] at a depth of 78 metres below Lake Constance, so the whole radiation may show this phenomenon. The absorption of the radiation has been studied in media other than water by K. Büttner,[99] E. Steinke,[1] G. Hoffman,[2] and L. Myssovski and L. Tuvim.[3] The importance of analysing the absorption curves into two, representing the primary and the degraded radiation, has been emphasised by L. H. Gray[4] and H. Kuhlenkampff.[5]

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[94] *Ann. Reports*, 1928, **25**, 321.

[95] *Z. Physik*, 1929, **56**, 751; *Nature*, 1929, **123**, 638; *A.*, 1929, 621.

[96] *Naturwiss.*, 1929, **11**, 183.

[97] *Z. Physik*, 1928, **50**, 808; *Nature*, 1930, **126**, 57.

[98] *Sitzungsber. Akad. Wiss. Wien*, 1928, [2 *A*], **137**, 327.

[99] *Z. Geophysik*, 1927, **3**, 161.

[1] *Z. Physik*, 1927, **42**, 570; 1928, **48**, 647.

[2] *Physikal. Z.*, 1925, **26**, 669; *Ann. Physik*, 1927, [iv], **82**, 413; *A.*, 1927, 289.

[3] *Z. Physik*, 1928, **50**, 273; *A.*, 1928, 1070.

The Fine-structure Constant, the Proton, and the Electron.

(Sir) A. S. Eddington[6] has called attention to the possibility that the reciprocal of the " fine-structure constant," $2\pi e^2/hc$, which is known to be dimensionless, is integral and equal to 137. The starting point of this work is the observation that the interaction of electrons can now be described by two principles : Coulomb's electrostatic forces and Pauli's exclusion principle. If these are regarded as two aspects of the same feature of our world, there must necessarily be a theoretical connexion between the two constants e^2 and $hc/2\pi$ which they respectively introduce. His first view was that the ratio should be simply the number of symmetrical terms in an array of 16 rows and 16 columns, which is 136. Since the experimental value of the ratio is $137{\cdot}29 \pm 0{\cdot}11$, the theory suggested that possibly the value of e was about 0·5% too small, a suggestion that did not escape comment from those[7] who upheld R. A. Millikan's[8] value as against one determined by a new X-ray method due to E. Bäcklin[9] which is approximately right for the theory. Eddington discovered later,[10] however, that in addition to the 136 symmetrical degrees of freedom there was one characteristic of a pair of electrons which, unlike the others, has no analogue in the theory of a single electron, namely, an alteration of the proper distance between them ; this degree of freedom had been overlooked through his not recognising its distinctness from the others. The most probable values of the e, h, c, N, and other fundamental constants have been discussed by R. T. Birge[11] and R. A. Millikan,[8] and given as $e = 4{\cdot}770 \pm 0{\cdot}005 \times 10^{-10}$ abs.e.s.u., $h = 6{\cdot}547 \pm 0{\cdot}011 \times 10^{-27}$ erg./sec., $c = 2{\cdot}99796 \pm 0{\cdot}00004 \times 10^{10}$ cm. sec.$^{-1}$, and $N = 6{\cdot}064 \pm 0{\cdot}006 \times 10^{23}$. From an examination of the evidence available, they conclude that the ratio $hc/2\pi e^2$ cannot be an integer. The value of Eddington's suggestion (which necessarily requires an integral value for the ratio) thus depends upon the accuracy with which e can be determined, since the value for

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[4] *Proc. Roy. Soc.*, 1929, [*A*], **122**, 647; *A.*, 1929, 372.

[5] *Sitzungsber. Akad. Wiss. Wien*, 1928, [2 *A*], **137**, 327.

[6] *Proc. Roy. Soc.*, 1929, [*A*], **122**, 358; *A.*, 1929, 231.

[7] R. T. Birge, *Nature*, 1929, **123**, 318; *A.*, 1929, 368; E. Bäcklin, *ibid.*, p. 409; *A.*, 1929, 369; J. H. J. Poole, *ibid.*, p. 530; *A.*, 1929, 484.

[8] *Physical Rev.*, 1930, [ii], **35**, 1231; *A.*, 977.

[9] *Diss.*, Uppsala, 1927.

[10] *Nature*, 1929, **124**, 840; *A.*, 10; *Proc. Roy. Soc.*, 1930, [*A*], **126**, 696; *A.*, 518.

[11] *Physical Rev., Suppl.*, 1929, **1**, 1.

h happens to be also dependent upon that of e. The new X-ray method of E. Bäcklin [9] promises a very accurate value, but his own determination of e by it is not regarded as very accurate. A. P. R. Wadlund,[12] however, using this method, has obtained a few values the mean of which, $4{\cdot}774 \pm 0{\cdot}007 \times 10^{-10}$, is close to Millikan's. The value $4{\cdot}775 \times 10^{-10}$, which is not outside the limits of these determinations, gives with the present accepted values of the other constants the value required by Eddington's theory. It may be pointed out that a form of this ratio had earlier been employed by G. N. Lewis and E. Q. Adams [13] in their theory of absolute units. There it was regarded as being equal to $8\pi(8\pi^5/15)^{1/3}$, the numerical value of which is 137·35.

The ratio, M/m, of the masses of the proton and the electron is another dimensionless constant which has attracted attention. J. Perles [14] has found that this ratio may be expressed as $hc(\pi - 1)/e^2$. This gives a value 1847·4, identical with the best experimental value, *viz.*, 1847 ± 2. R. Fürth [15] has shown that the value of the ratio follows from general quantum considerations, and gives a formula which leads to a value of 1836. E. E. Witmer [16] has pointed out that it is very nearly the square of half the atomic number of the heaviest known inert gas (*i.e.*, 1849), an agreement which it is difficult to regard as more than a coincidence. He expresses the relation between the masses and the atomic numbers of helium and hydrogen as $M_{\mathrm{He}}/M_{\mathrm{H}} = (Z_{\mathrm{He}}/Z_{\mathrm{H}})^2[1/(1 + \alpha)]$, where M represents mass and Z atomic number, and α is $2\pi e^2/hc$. The value of $hc/2\pi e^2$, calculated from this equation, *i.e.*, 138·1, is close to the experimental value, 137·29.

A more developed theory on this subject has been put forward by (Sir) A. S. Eddington.[17] He proposes a theory of mass in which the representation in a microscopic space–time increases the natural mass of the proton in the ratio $136/\sqrt{10}$ and diminishes that of the electron in an equal ratio. This gives $M/m = 136^2/10 = 1849{\cdot}6$ which is close to the experimental value. He also shows that if electrons and protons form a perfectly rigid system, the mass M relative to that of its constituents is reduced in the ratio 136/137. This ratio agrees approximately with the reduction of the mass of a proton when it enters into a nucleus. Its reciprocal, in fact (1·00735), is intermediate between the atomic weight of hydrogen expressed in terms of He = 4 (1·00724) and O = 16 (1·00778): better agreement than this cannot be expected on the assumptions made.

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[12] *Proc. Nat. Acad. Sci.*, 1928, **14**, 588; *Physical Rev.*, 1928, [ii], **32**, 841; *A.*, 1929, 227.

[13] *Ibid.*, 1914, [ii], **3**, 92.

[14] *Naturwiss.*, 1928, **16**, 1094.

[15] *Ibid.*, 1929, **17**, 688, 728; *A.*, 1929, 1123, 1209.

[16] *Nature*, 1929, **124**, 180; *A.*, 1929, 973.

[17] *Proc. Camb. Phil. Soc.*, 1931, (in press).

A novel theory of protons and electrons has been proposed by P. A. M. Dirac.[18] The relativity quantum theory of an electron leads to a wave-equation which has solutions corresponding with negative energies, the energy of an electron being regarded as positive. If a negative-energy electron is regarded as a proton, several paradoxes arise. This difficulty is escaped by postulating only one fundamental particle, the electron. The stable states of an electron are those of lowest energy. In consequence, all electrons would tend to fall into the negative-energy states with emission of radiation were it not for Pauli's exclusion principle, which prevents more than one electron going into any one state. Dirac, however, assumes that there are so many electrons in the world that all the states of negative energy except perhaps a few are occupied, and supposes that the infinite number of electrons present in any volume will remain undetectable if they are uniformly distributed. Only a few " holes " or missing states of negative energy consequently remain amenable to observation, and these holes, these things of positive energy, are identified with the protons. Various obvious difficulties which follow this conception are dealt with in the theory. One, however, remains, *viz.*, the difficulty of explaining why the proton and the electron differ so widely in mass. According to this theory, they should be of equal mass or, by considering interaction, of slightly different masses. J. R. Oppenheimer [19] attempts to surmount some of the difficulties in the foregoing theory by supposing that all, and not merely nearly all, of the states of negative energy are occupied, so that a positive-energy electron can never make a transition to a negative-energy state. This implies, however, that there are no holes which can be called protons, so that the proton has to be regarded as a particle independent of the electron. In consequence, the proton will have its own negative-energy states which must be assumed to be all occupied. The independence of the proton and electron allows them to have any relative mass they require, but it is inconsistent with the possibility that a proton can annihilate an electron.

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[18] *Proc. Roy. Soc.*, 1930, [*A*], **126**, 360; *A.*, 271. *Nature*, 1930, **126**, 606.

[19] *Physical Rev.*, 1930, [ii], **35**, 461, 939; *A.*, 660, 836.

THE ELECTRICAL CONDUCTIVITY OF SOLUTIONS.

For nearly forty years the Arrhenius theory of ionic dissociation was the centre of controversy among electro-chemists. While its main principle, that the variation of the equivalent conductivity of a solution depends solely on a variation in the proportion of ionised molecules, was supported by the behaviour of weak electrolytes, it was shown to be incompatible with the behaviour of strong electrolytes, and the discrepancies between theory and fact led in 1907 to G. N. Lewis's [1] empirical conception of the activity coefficient to replace the Arrhenius degree of dissociation, $\alpha = \Lambda_c/\Lambda_0$. From time to time a number of investigators (J. J. van Laar,[2] W. Sutherland,[3] N. Bjerrum,[4] and others) suggested that strong electrolytes were completely ionised, and that the variations of their properties with dilution might be due to the electrical forces between the ions. S. R. Milner [5] in 1912 was, however, the first to see that the solution of the problem was to be found in the effect of the Coulomb forces in preventing the random distribution of the ions. It was not until 1923 that P. Debye and E. Hückel [6] devised a relatively simple mathematical treatment of the problem yielding a general solution, which they applied to the theory of the conductivity of an electrolyte. By finding methods of calculating the activity coefficient of an electrolyte and the change in its electrical conductivity with dilution from the physical properties of the solvent and the concentration, they opened up a new phase of development in the study of electrolytic solutions. They made it possible to calculate the behaviour in any solvent of an ideal completely dissociated electrolyte, if it were dependent solely on the physical properties of the solvent and of the ions, thereby enabling us to see to what extent a particular electrolyte deviates from ideal behaviour and how far chemical influences come into play.

The report deals chiefly with the following topics :

(1) A sketch of the Debye–Hückel–Onsager theory.
(2) The verification of this theory by conductivity measurements at high frequencies.
(3) Recent work on conductivity in water and non-aqueous solvents, and a comparison of the results with the Debye–Hückel–Onsager theory.
(4) Ionic mobilities in various solvents.
(5) Solvation of ions and its relation to ionic association.

The main object of the report is to show how far the Debye–Hückel theory is in accord with the results of conductivity measurements, and as the theory can only be strictly true in dilute solutions, experimental work in the range $0{\cdot}002N$ to $0{\cdot}0001N$ has been chiefly considered. Also, as there has been no systematic work on multivalent ions in non-aqueous solvents, consideration has been practically limited to uni-univalent electrolytes.

The report deals chiefly with researches carried out between 1920 and 1930, and, apart from the earlier work in water, greater reliance can be placed on the results of more recent work owing to the great improvements in technique. It is obviously impossible to include references to all the researches which have been done in this field during the last decade, but an attempt has been made in the section dealing with ionic mobilities and transport numbers to indicate the existence of serious discrepancies and gaps. In spite of the many additions that have been made to our knowledge of non-aqueous solutions in recent years, much still remains to be done in this field before we have a picture of the properties of electrolytic solutions which is in any way complete or definitely established.

The most important recent compilation of conductivity data is contained in P. Walden's three volumes, "Das Leitvermögen der Lösungen." [7] Monographs dealing with different aspects of the problem have been published by C. A. Kraus,[8] R. Lorenz,[9] H. Ulich,[10] H. Remy,[11] and C. W. Davies.[12] There are also the Report of the Discussion of Strong Electrolytes held by the Faraday Society in Oxford in 1927,[13] and separate papers dealing with the general position by H. Ulich and E. J. Birr,[14] N. Bjerrum,[15] and R. Schingnitz.[16]

The Theory of Debye and Hückel.

The Ionic Atmosphere.—The basis of the Debye–Hückel theory of the properties of electrolytic solutions is the idea of an ionic atmosphere suggested by S. R. Milner,[5] who pointed out that the distribution of the ions of an electrolyte round a given ion would not be random as is the distribution round a fixed point in the solution. Owing to the Coulomb forces there will be an excess of positive ions in the neighbourhood of a negative ion and *vice versa.* The density of charge in a small element of volume at a certain distance from the central ion will fluctuate, and the density of charge at this point is taken as the mean density averaged over an interval of time. Thus on a time average each ion can be considered as surrounded by a spherical ionic atmosphere, the density of which will decrease with the distance from the ion. The ionic atmosphere will affect the electrical potential of the surface of the central ion, and, by taking into account the changes of potential with dilution, Milner was able to calculate the freezing-point depression of an electrolyte at different dilutions, assuming that it was completely dissociated. Debye and Hückel[6] greatly simplified the mathematical treatment of the problem by applying Poisson's equation to the distribution of charge in the ionic atmosphere.

Since a solution as a whole is electrically neutral, the total charge of the ionic atmosphere is equal and opposite to that of the central ion, and its distribution will vary with the nature and concentration of the electrolyte and with the dielectric constant of the solvent. Debye and Hückel found the following expression for $\bar{\psi}$, the mean electric potential at a point ion due to its atmosphere :

$$\bar{\psi} = -\frac{z\varepsilon\kappa}{D} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where $-\varepsilon$ is the charge on an electron, z the valency of the ion with the sign of the charge on the ion, D the dielectric constant of the pure solvent, and $1/\kappa$ is a length which is characteristic of the rate of decrease of the density of the atmosphere with the distance from the central ion. Its value for binary electrolytes is given by

$$1/\kappa = \frac{1{\cdot}985 \times 10^{-10}}{z}\sqrt{\frac{DT}{c}} \text{ cons.} \quad . \quad . \quad . \quad . \quad (2)$$

where T is the absolute temperature and c the concentration in mols. per litre. The characteristic length $1/\kappa$ is often called the radius of the ionic atmosphere; since on comparing equation (1) with the expression for the potential at a distance r from a point charge $z\varepsilon$, *viz.*, $z\varepsilon/Dr$, it is seen that the potential due to the ionic atmosphere is equivalent to that of a charge $z\varepsilon$ uniformly distributed on the surface of a sphere of radius $1/\kappa$ surrounding the central ion, so that the two together are equivalent to a double layer of charge $z\varepsilon$ and thickness $1/\kappa$. In water at 25° for a uni-univalent electrolyte $1/\kappa = 3 \times 10^{-8}/\sqrt{c}$ cm., and in $0{\cdot}01N$ solution $1/\kappa = 30 \times 10^{-8}$ cm. while the mean distance between the ions is 44×10^{-8} cm. From equation (2) it will be seen that the radius of the ionic atmosphere varies inversely with the square root of the concentration, and this accounts for the fact that such diverse properties of solutions as activity coefficients and equivalent conductivities are found to be functions of $\sqrt{c}$. The effect of the atmosphere on the properties of the ion will naturally depend on $1/\kappa$, and equation (2) shows that this will diminish in concentrated solutions and in solvents of low dielectric constant.

The Effect of the Ionic Atmosphere on the Ionic Mobility.—The conductivity of a solution depends on the number of ions that it contains and on their mobility. The classical theory of Arrhenius considers the effect of ionic dissociation on the former factor, whilst the Debye–Hückel theory considers the effect of the interionic forces on the latter.

If an ion moves in a solution under the influence of a uniform potential gradient, it reaches a steady state of motion in which the electric force acting on it is in equilibrium with the viscous force opposing its motion. Debye and Hückel showed that both these forces are modified by the ionic atmosphere.

When an ion is stationary its atmosphere has central symmetry, but when it moves in an external field the atmosphere will no longer remain symmetrical owing to the fact that its formation or disappearance occupies a finite time, in consequence of which the electric force acting on the ion will be altered.

Debye and Hückel investigated, by means of the equations for the Brownian movement, the rate of decrease of the density of the atmosphere if the central ion is removed, and they express this rate in terms of an essential time constant τ which they call the time of relaxation of the atmosphere. To a first approximation, the radius of an atmosphere is doubled during the time of relaxation τ, which, for an electrolyte like potassium chloride with ions of equal mobility, is given by the expression

$$\tau = \frac{\rho}{\kappa^2 kT} \text{ seconds} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where k is the Boltzmann constant and ρ is the frictional constant of the ion, defined as the force opposing an ion moving with unit velocity, and is given by $\rho = 1{\cdot}5 \times 10^{-7}/l_0$. For a potassium chloride solution in water at 25° containing c mols. per litre this gives $\tau = 0{\cdot}55 \times 10^{-10}/c$ secs.

When an ion moves under an external potential gradient, it has continuously to build up a fresh atmosphere in front of it while the atmosphere has to die out behind it; consequently the atmosphere in front of the ion will never reach its equilibrium density, while behind it the density will be above its equilibrium value. Since the charge density of the atmosphere has the opposite sign to the charge on the ion, the dissymmetry will reduce the external electrical force acting on the ion. Increase in the ionic velocity produces an increased dissymmetry, and the consequent reduction of the field intensity, which we may call the dissymmetry term, varies directly with the velocity for small velocities. The actual dissymmetry is small; for example, in an external field of 1 volt/cm., a potassium ion in a 0·001N-solution will move approximately through 7/100,000 of the radius of its ionic atmosphere during its time of relaxation, but even the slight dissymmetry thus produced is sufficient to cause an appreciable retardation of the ion owing to the relatively enormous size of the electronic charge.

The second way in which the ionic atmosphere influences the ionic mobility is due to the increased viscous resistance caused by the movement of the ions of the atmosphere in the opposite direction to the central ion. Since the ions are assumed to carry a certain amount of solvent with them, the viscous resistance to ionic motion is greater than if the solvent were at rest. Debye and Hückel assume that the ordinary equations of motion in a viscous fluid hold right up to the surface of the ions where no slip occurs, and obtain an expression for the additional frictional force due to the ionic atmosphere, which, like the dissymmetry term, varies inversely with the radius of the ionic atmosphere and so is proportional to the square root of the concentration.

Colloid particles acquire a charge and a potential with respect to the solution and consequently migrate in an electric field. The phenomenon is called electrophoresis and is strictly analogous to the migration of ions in an electric field, since the ion and its atmosphere are equivalent to a diffuse double layer of thickness $1/\kappa$, which is the exact counterpart of the diffuse portion of the double layer round the colloid particle. The main difference is that the charge on the colloid particle is due to adsorption, and in general alters with the concentration. Owing to the similarity between the two phenomena, Debye and Hückel call the additional frictional force the electrophoretic term.

Both these effects due to the ionic atmosphere reduce the mobility of the ion below its value at infinite dilution, and from their calculations Debye and Hückel arrived at the following equation for the variation of the equivalent conductivity of a z-valent binary electrolyte in a solvent of dielectric constant D at a temperature T,

$$\frac{\Lambda_0 - \Lambda_c}{\Lambda_0} = \left\{\frac{K_1}{(DT)^{3/2}} \cdot w_1 + \frac{K_2}{(DT)^{1/2}} w_2 b\right\}\sqrt{2c} \quad . \quad (4)$$

where the first and second terms on the right-hand side are the dissymmetry and electrophoretic terms respectively, K_1 and K_2 are universal constants, w_1 and w_2 are valency factors, and b is the average radius of the ions. This reduces to the form

$$\Lambda_c = \Lambda_0 - x\sqrt{c} \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

which is identical with the empirical equation used by Kohlrausch for the conductivities of dilute aqueous solutions. Comparison with experimental results shows that the coefficient of $\sqrt{c}$ in equation (4) is of the right order of magnitude if a value is assumed for the ionic radii of 10^{-8} cm. in accordance with X-ray data. But if the value of b is calculated from the ionic mobilities at infinite dilution, assuming Stokes's law to hold, the observed and calculated coefficients are not in exact agreement; *e.g.*, for potassium chloride solutions in water at 25° they are 0·461 and 0·547 respectively.

Onsager's Modification of the Debye–Hückel Theory of Conductivity.—L. Onsager [17, 18] pointed out that Debye and Hückel, in calculating the retardation of an ion due to the dissymmetry of the atmosphere, had considered the dissymmetry round an ion which moved with a constant velocity in the solution and had neglected its Brownian movement. Onsager recalculated the value of the dissymmetry term, taking into account this effect, and found that for a uni-univalent electrolyte a correcting factor of $2 - \sqrt{2} = 0{\cdot}586$ must be introduced into Debye and Hückel's dissymmetry term. He also reinvestigated the electrophoretic effect and showed that its magnitude in dilute solutions was independent of any assumption as to the validity of Stokes's law in the immediate neighbourhood of the ions. The electrophoretic term has been the subject of further papers by Debye and Hückel,[19] who investigated it with special reference to the electrophoresis of colloid particles.

Onsager's final equation has the same general form as Debye and Hückel's, and when numerical values are inserted for the universal constants, it becomes for a z-valent binary electrolyte

$$\Lambda_c = \Lambda_0 - \left[\frac{0{\cdot}986 \times 10^6}{(DT)^{3/2}}(2 - \sqrt{2})z^2\Lambda_0 + \frac{58{\cdot}0}{(DT)^{1/2}\eta}z\right]\sqrt{2zc} \qquad (6)$$

where η is the viscosity of the solvent.

For various solvents at 25° this equation becomes for uni-univalent electrolytes :

For water $\Lambda_c = \Lambda_0 - (0{\cdot}228\Lambda_0 + 59{\cdot}8)\sqrt{c}$
,, methyl alcohol $\Lambda_c = \Lambda_0 - (0{\cdot}957\Lambda_0 + 158{\cdot}1)\sqrt{c}$
,, ethyl alcohol $\Lambda_c = \Lambda_0 - (1{\cdot}256\Lambda_0 + 87{\cdot}8)\sqrt{c}$

For sodium chloride in each solvent these equations become :

For water $\Lambda_c = 126{\cdot}4 - (28{\cdot}8 + 59{\cdot}8)\sqrt{c}$
,, methyl alcohol $\Lambda_c = 97{\cdot}0 - (93 + 158{\cdot}1)\sqrt{c}$
,, ethyl alcohol $\Lambda_c = 43{\cdot}0 - (54 + 87{\cdot}8)\sqrt{c}$

These equations show that the dissymmetry term and the electrophoretic term (the first and second coefficients of $\sqrt{c}$ respectively) are of the same order, but their relative magnitude varies with the properties of the solvent and with the ionic velocities of the ions present.

Limitations and Developments of the Theory of Debye and Hückel.—

The simple Debye and Hückel theory involves certain assumptions and approximations which have been the subject of subsequent investigations. These have been concerned mainly with the limits in which the theory might be expected to hold and with attempts to adapt it to higher concentrations, but the equations have not yet been applied to the conductivity problem.

All subsequent work has gone to show that the limiting equation (1) is correct for high dilutions, but that it might be expected to break down, even if allowance is made for the size of the ions and for higher-order terms, when the potential energy of the ions due to their atmospheres becomes comparable with their kinetic energy of translation. According to H. A. Kramers [20] and to R. H. Fowler,[21] this occurs at about 0·01*N* for aqueous solutions of uni-univalent salts at 25°, and at lower concentrations when the interionic forces are increased owing to the higher valency of the ions or to a lower dielectric constant of the solvent, *e.g.*, at *N*/600 for uni-univalent salts in methyl alcohol.

The physical assumptions underlying the theory may be summarised as follows :

(i) That all forces other than Coulomb forces between the ions can be neglected.
(ii) That corrections for the overlapping of the ionic atmospheres can be neglected.
(iii) That the solvent between the ions behaves like the pure solvent in bulk.

The first assumption implies that the theory applies to an ideal electrolyte which is completely dissociated into point ions. Debye and Hückel made allowance for a mean distance of closest approach of the ions, but experimental values for this additional constant were subsequently shown by O. Schärer [22] to be negative for dilute solutions of thallous chloride in dilute aqueous thallous nitrate. The reason for this anomaly is the neglect of terms other than those of the first order in the derivation of equation (1), since these become significant at concentrations where the effect of the ionic size is important.

R. H. Fowler,[21] while investigating the second assumption, showed that the neglect of the higher-order terms was equivalent to assuming that the potential energy of an ion, due to the field and atmosphere of another ion, is small compared to its kinetic energy of translation. The overlapping of ionic atmospheres can, however, be overlooked if the potential of an ion due merely to the atmosphere of another ion is small compared to its kinetic energy of translation, which is a less stringent condition. H. Müller [23] and T. H. Gronwall [24] have considered the effect of the size of the ions on their activity coefficients, and T. H. Gronwall, V. K. LaMer, and K. Sandved[25] have carried out a solution of the fundamental equations of Debye and Hückel as far as terms of the fifth order for binary electrolytes. Their results give reasonable values for the ionic radii and also confirm the view that there is a greater probability of finding an ion in a region where its potential energy is great compared with its kinetic energy, than would have been predicted by the Debye–Hückel theory. As a result, the radius of the ionic atmosphere will be reduced and the properties of the solution so modified that, if compared with the simple theory, the electrolyte will appear to be incompletely dissociated. Bjerrum[26] had previously attacked the problem of ionic association* by considering the effect of the limiting distance, to which two ions can approach one another, on the probability of the formation of an ion pair, which would be equivalent to an undissociated molecule without involving the formation of a covalent linkage.

The use of the macroscopic dielectric constant of the solvent has been justified by P. Debye and L. Pauling[27] for sufficiently dilute solutions, and a similar justification has been made by Onsager[17] as regards the viscosity. Hückel[28] has investigated the effect of the variation of the dielectric constant with concentration and of the deformability of the ions. The intense pressures set up owing to the electrostatic attraction of the polarisable and dipolar solvent molecules by the ions and the possibility of electric saturation round the ions have been considered from different points of view by H. Schmick,[29] T. J. Webb,[30] F. Zwicky,[31] and Debye.[32]

Conductivity at High Frequencies and High Electromotive Forces.

The essential correctness of the view that there exists an ionic atmosphere, requiring a finite time for its establishment or dissipation, has been strikingly confirmed by recent work on the variation of the conductivity of solutions both at high frequencies and at high electromotive forces.

According to the Debye–Hückel theory, the ionic atmosphere, owing to its time of relaxation, lags behind an ion moving with a steady velocity, and therefore produces a retarding force. If the applied electromotive force is an alternating one with a long period, the atmosphere still lags behind during the whole of the oscillation except for a short time at either end when the ion reverses the direction of its motion. At higher frequencies the amplitude of the oscillations of the ion and of the atmosphere both become small. P. Debye and H. Falkenhagen[33] showed that, owing to this, the dissymmetry term should decrease to zero as the frequency increases to infinity, the effect first being appreciable when the period of oscillation reaches the order of magnitude of the time of relaxation of the atmosphere.

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* The term association is used throughout this Report to imply any modification of the state or configuration of the ions, which involves a decrease in the conductivity. This may be due either to the formation of a covalent linkage between them or to a modified distribution of the ions, leading in the extreme case to the formation of an ion pair as suggested by Bjerrum.

It would therefore be expected that the conductivity of a solution should vary with the frequency of the current. But the investigation of this phenomenon is complicated because alternating electromotive forces produce both a real and a capacity current. Both increase[33] with the frequency, the former appearing as an increase in the conductivity, and the latter as an increase in the dielectric constant of the solution. Unfortunately, existing experimental methods are inadequate for the detection of this latter effect.

On the other hand, the increase in conductivity with the frequency has been measured by H. Sack[34] and H. Zahn[35] and their co-workers, as well as by A. Deubner.[36] Owing to the need to distinguish between real and capacity current, the most convenient method is to adjust the concentrations of two solutions until their behaviour at a high frequency is identical, and then to compare their conductivities at a low frequency. Results have been obtained for aqueous solutions by comparing in this way (i) salts of different valency types, and also (ii) salts with acids, since these are affected differently by change of frequency owing to the high mobility of the hydrogen ion. Solutions of copper sulphate were compared with solutions of potassium chloride possessing the same high-frequency conductivity at a wave-length of 16 metres in air, and at low frequencies their conductivities showed a maximum difference of $1{\cdot}7 \pm 0{\cdot}15\%$ when the concentration of the copper sulphate was $0{\cdot}0012N$. The general result of the experiments is in satisfactory agreement with theory. Zahn,[37] working at a wave-length of 4·5 cm., considers that he has obtained evidence against Hückel's theory of the mobility of the oxonium ion $[H_3O]^{\cdot}$.

M. Wien and co-workers[38] have observed that electrolytic solutions do not obey Ohm's law under high potential gradients. G. Joos and M. Blumentritt[39] showed that this phenomenon could be interpreted in terms of the time of relaxation of the ionic atmosphere. In a potential gradient of 500,000 volts/cm., the ions in a $0{\cdot}001N$-solution of potassium chloride in water at 25° would move through a distance equal to 35 times the radius of their atmospheres during the time of relaxation. The ions would therefore become separated from their atmospheres and, in the limit, their mobilities would have the same values as at infinite dilution. The effect of increasing the potential gradient should vary with salts of different valency types, and this was tested experimentally by comparing the resistances of solutions of salts such as magnesium sulphate and sodium chloride under different potential gradients. The results were found to be in general agreement with theory.

Additional evidence for the existence of a time of relaxation of the atmosphere has been obtained from a study of the viscosity of aqueous solutions. G. Jones and M. Dole[40] concluded that, as a result of the interionic forces, the viscosity of all electrolytic solutions must be greater than that of the pure solvent at high dilutions, although certain salts, such as potassium chloride or nitrate, are known to lower the viscosity of water. H. Falkenhagen and M. Dole[41] later obtained a quantitative expression for the relative viscosity of dilute solutions in the special case of a binary electrolyte whose ions have equal mobilities, their calculation being based on the time of relaxation of the ionic atmosphere. W. E. Joy and J. H. Wolfenden[42] have recently shown that the viscosity of aqueous solutions of potassium chloride at concentrations below $0{\cdot}02N$ is greater than that of pure water and that the effect is of the calculated order.

Recent Conductivity Measurements and a Comparison of the Results with the Debye–Hückel–Onsager Theory.

The following sections deal with the results of conductivity measurements in twelve solvents in which dilute solutions have been investigated. The percentage deviations of a number of typical electrolytes from the Debye–Hückel–Onsager theory will be found on p. 342, where they are collected so as to facilitate a comparison of the results in different solvents. The differences between the observed and calculated values of x in equation (5) are, of course, dependent on the values assigned to the dielectric constants of the solvents, as to which there are often serious discrepancies between the results of different authors. A greater measure of agreement as regards these constants would be a great help to workers in this field.

In water there is a rather sharp contrast between weak electrolytes (acids and bases) and uni-univalent salts, all of which are strong electrolytes. It will be seen that in non-aqueous solvents this difference disappears, for even uni-univalents salts may be medium or weak electrolytes. Their nature is shown qualitatively at once by the form of the $\Lambda_c/\sqrt{c}$ graphs as compared with the theoretical line for each electrolyte.

Methods of Conductivity Measurement.—The Ostwald method of successive dilution for determining the conductivity is subject to the possibility of large errors in dilute solutions, owing to the uncertainty of the solvent correction and the cumulative experimental error. This method has been abandoned by most investigators in favour of that first proposed by W. C. D. Whetham,[43] and used by F. Kohlrausch and M. E. Maltby,[44] in which a number of successive additions of strong solution are made to the pure solvent in the conductivity cell. The resistances of the solutions are always measured by the Kohlrausch method, and much attention has been paid, particularly in America, to refinements in the apparatus. The elimination of various errors due to the use of alternating current has been discussed at length by E. W. Washburn,[45] S. F. Acree,[46] J. L. R. Morgan and O. M. Lammert,[47] G. Jones and R. C. Josephs,[48] and T. Shedlovsky.[49] A thermionic valve oscillator is now generally used as a source of alternating current of symmetrical wave form ; suitable types are described by R. E. Hall and L. H. Adams,[50] H. Ulich,[51] J. W. Woolcock and D. M. Murray-Rust,[52] and by Grinnell Jones and G. M. Bollinger.[53]

The design of conductivity cells has been discussed by E. W. Washburn,[45] and their treatment by Morgan and Lammert.[47] Suitable forms for dilute solutions have been described by H. Hartley and W. H. Barrett,[54] by C. A. Kraus and H. C. Parker,[55] and by H. C. Parker,[56] and the design of a conductivity cell for eliminating electrode effects has recently been published by T. Shedlovsky.[57] The determination of cell constants has been studied by H. C. Parker and E. W. Parker [58] and by M. Randall and G. N. Scott.[59] A useful summary of experimental methods is given by C. W. Davies.[12]

Water.—A number of uni-univalent salts were measured in water by F. Kohlrausch and few later measurements have been made. P. Walden and H. Ulich [60] repeated some of the work at 18° and extended it to measurements at 0° and 100° in order to see whether the product of the equivalent conductivity and the viscosity of the solution is constant over a range of temperature. Their values at 18° are in good agreement with Kohlrausch's except for potassium and lithium perchlorates, so that the mobility of the perchlorate ion is in doubt.

H. J. Weiland [61] measured the conductivity of potassium chloride in very dilute solution, and his values are in reasonable agreement with those of Kohlrausch and of Walden in the range where they overlap. In view of the great difficulty of obtaining trustworthy data at the extreme dilutions at which he worked, and of his questionable method of extrapolation to Λ_0, his claim that the results are in accordance with the Ostwald dilution law at high dilutions cannot be sustained, quite apart from the fact that no allowance is made for the change of mobility with concentration.

Kohlrausch[62] has shown that the conductivities of all the salts investigated by him in water obey the relation $\Lambda_c = \Lambda_0 - x\sqrt{c}$, and Onsager[18] has compared the values of x found by Kohlrausch with those calculated by equation (6), and finds that there is reasonable agreement for most uni-univalent salts, the average deviation from theory being about 7%. The observed values of x in most cases are slightly greater than the theoretical values, the largest differences being found for the nitrates. The values given on p. 342 are mainly for salts that have been measured in other solvents, and the general agreement is closer than those figures would suggest. Lithium picrate appears to give an unusually large negative deviation. The values for bi-univalent salts are also in fair agreement, (± 15%), showing that the valency factors in the Debye–Hückel–Onsager equation are correct. Bi-bivalent salts give experimental values of x which are considerably greater than the calculated values, pointing to ionic association, and C. W. Davies[63] has calculated dissociation constants for these salts.

Methyl Alcohol ($D = 30{\cdot}3$).—H. Goldschmidt's measurements were largely concerned with the conductivities of acids,[64] which are dealt with in a later section. He also measured a small number of salts by the Ostwald method of dilution.[65] P. Walden, H. Ulich, and F. Laun[66] measured a number of salts with organic kations at 0°, 25°, and 50°, and their results are discussed in the section dealing with Walden's rule. J. E. Frazer and H. Hartley[67] have measured the conductivity of uni-univalent salts over a range of concentrations from $N/10{,}000$ to $N/500$, and this work has been extended to the thiocyanates by A. Unmack, D. M. Murray-Rust, and H. Hartley[68] and to the perchlorates by E. D. Copley and Hartley.[69] All the uni-univalent salts obey the square-root relation and the experimental values of x agree well in many cases with those calculated theoretically, but the individual differences are often greater than in water, *e.g.*, for silver nitrate, which is associated even at high dilutions. In some cases, $x_{\text{obs.}}$ is slightly less than $x_{\text{calc.}}$, but the latter values depend on the number used for the dielectric constant of the solvent, and if a larger value than 30·3 were used for the calculation, the value of $x_{\text{calc.}}$ would be smaller. A comparison of the results for the chlorides, nitrates, and thiocyanates of the alkali metals shows that the deviations from Onsager's equation increase with the atomic number of the metal.[68] The mobilities of the kations increase in the same order, and, if they are assumed to vary inversely with the sizes of the solvated ions, it appears that for strong electrolytes in methyl alcohol the divergence from the theoretical behaviour is greatest for kations of small diameter in solution.

L. Thomas and E. Marum [70] have recently measured some uni-univalent salts in methyl alcohol at high dilutions. They find a linear relation between Λ_c and $\sqrt{c}$, but the slopes of their lines are greater than those found by Frazer and Hartley and their values of Λ_c are from 2 to 3% higher.

Ethyl Alcohol ($D = 25$).—The results of Goldschmidt [64, 71] and of Walden, Ulich, and Laun [66] for ethyl alcohol are also dealt with later, as the scope of their investigations is similar to that in methyl alcohol. The values quoted by Ulich [10] for metallic salts are mainly taken from early work by Dutoit, Turner, and others, but Thomas and Marum [70] and Copley, Murray-Rust, and Hartley [72] have recently published results for a small number of salts in ethyl alcohol, and a continuation of the latter work by M. Barak [73] extends to a large number of uni-univalent salts. An examination of the results in the light of the Debye–Hückel–Onsager equation shows that ethyl alcohol is similar to methyl alcohol, as nearly all the salts conform to the linear relation $\Lambda_c = \Lambda_0 - x\sqrt{c}$. The differences between the observed and calculated values of x are rather greater than in methyl alcohol, and in no case is $x_{\text{obs.}}$ less than $x_{\text{calc.}}$ If the lower value of 23, given by C. P. Smyth and W. N. Stoops [74] for the dielectric constant, were used in the determination of $x_{\text{calc.}}$, the agreement with the theory would be closer. The results show that the general tendency for ionic association to take place is rather greater in ethyl than in methyl alcohol, as would be expected from the lower dielectric constant of the former. The dependence of the degree of divergence of a salt from ideal behaviour on the nature of the kation is similar to that in methyl alcohol, as in each series of salts of the alkali metals the deviation increases steadily from lithium to cæsium.

Nitromethane ($D = 37$).—Walden [75] and J. C. Philip and H. R. Courtman [76] measured tetraethylammonium and potassium iodide in this solvent, and later J. C. Philip and H. B. Oakley [77] extended the measurements with potassium iodide over a wide temperature range. Further work has been done by C. P. Wright, Murray-Rust, and Hartley.[78] Ionic association takes place to a much greater extent in nitromethane than in either of the alcohols, in spite of its higher dielectric constant. None of the salts with metallic kations give a linear relation between Λ_c and $\sqrt{c}$ over the range 0·002 to 0·0001*N* and, where there is a linear portion of the curve, the slope is much greater than that calculated from Onsager's equation. The influence of the nature of the kations on the degree of association is opposite to that in the alcohols. This is illustrated by the behaviour of the thiocyanates : the potassium salt is a fairly strong electrolyte, sodium thiocyanate is of intermediate strength, while lithium thiocyanate is a weak electrolyte, the degree of dissociation at $N/1000$ being as low as 12%. The nature of the anion also has a large influence, the perchlorates being much less associated than the thiocyanates.

The tetraethylammonium salts, on the other hand, conform to the square-root relation, and the experimental values of x are in close agreement with those calculated theoretically, the nature of the anion having little effect on the behaviour of the electrolyte.

The difference in behaviour of nitromethane and hydroxylic solvents may be due to the fact that the former, having a purely donor character, can only form co-ordinate links with the kations, while the hydroxylic solvents can form links both with the kations and with the anions.

Acetonitrile ($D = 36$).—The most important work in this solvent is that of Walden and E. J. Birr,[79] who measured a large number of organic salts and a few with metallic kations. The behaviour of salts in this solvent is similar to that in nitromethane, as would be expected from the fact that their dielectric constants are nearly equal and that neither is a hydroxylic compound. Though the metallic salts conform to the linear relation $\Lambda_c = \Lambda_0 - x\sqrt{c}$, the experimental values of x are always greater than those calculated from equation (6). The picrates show that the influence of the kation on the degree of association in solution is also similar to that found for nitromethane, as the association increases in the order KPic, NaPic, LiPic, the lithium salt being only about 65% dissociated at $N/1000$. All the tetra-substituted ammonium salts are strong electrolytes, obeying the square-root relation, and many of them give values of x close to those calculated theoretically. The smallest values of $x_{\text{obs.}}$ are given by the tetrapropylammonium salts and they are in every case lower than the theoretical values. The deviations of the tetramethyl- and tetraethyl-ammonium salts are similar, though rather lower for the former. The mono-, di-, and tri-substituted ammonium salts are all considerably associated in acetonitrile, and the nature of the anion has a large influence on the degree of association, the picrates and iodides being much stronger electrolytes than the chlorides.

Nitrobenzene ($D = 34{\cdot}5$).—There are not many data for this solvent, but the results of Murray-Rust, H. J. Hadow, and Hartley [80] show that it is similar to nitromethane as an ionising solvent. Tetraethylammonium salts do not show large divergences from ideal behaviour, while silver perchlorate, the only metallic salt which has been measured, is appreciably associated in solution. The degree of association in every case is rather greater in this solvent than in nitromethane.

Benzonitrile ($D = 25{\cdot}2$).—A. R. Martin [81] has measured the conductivity of the iodides of lithium, sodium, potassium and tetraethylammonium, of lithium bromide, and of silver nitrate over a range of temperature from 0° to 70°. The first three salts give approximately straight lines when Λ_c is plotted against $\sqrt{c}$, although they are represented better by the empirical equation of A. Ferguson and I. Vogel,[82] *viz.*, $\Lambda_c = \Lambda_0 - Bc^n$, where n is not equal to $0{\cdot}5$: this equation is discussed later. The experimental values of x in the equation $\Lambda_c = \Lambda_0 - x\sqrt{c}$ are about twice as great as those calculated from Onsager's expression, so that these salts are not completely dissociated. Lithium bromide and silver nitrate are weak electrolytes, the degrees of dissociation at $N/1000$ being respectively about 44% and 50% at 25°. Tetraethylammonium iodide, however, obeys the square-root relation and, though it shows a considerable deviation from the ideal slope, it is the strongest electrolyte investigated.

Acetone ($D = 21$).—Walden, Ulich, and G. Busch [83] have measured a number of salts in this solvent, but, except for potassium and sodium iodides and lithium picrate, they are all salts with organic kations. Many of them give straight lines when Λ_c is plotted against $\sqrt{c}$, but the slopes of these lines are in every case greater than those calculated from Onsager's equation; the tetra-substituted ammonium picrates show the nearest approach to ideal behaviour, the smallest deviation being found for tetrapropylammonium picrate. N. L. Ross Kane [84] * has extended this investigation to a number of metallic salts and has also repeated some of Walden's measurements. Although there is fair agreement between the results for the tetraethylammonium salts in the two investigations, the values of Λ_c obtained by Ross Kane for the salts of the alkali metals are about 3% higher than those of Walden. For the picrates, thiocyanates, and iodides of the alkali metals the ionic association is greatest for the lithium salts and least for the potassium salts, so that in this respect acetone is similar to nitromethane as an ionising solvent; lithium thiocyanate and picrate (and also the chloride) are weak electrolytes in acetone, though the thiocyanate is rather stronger than in nitromethane. The perchlorates, however, are exceptional, for none of them is highly associated and the degree of association, as measured by the deviation of the slope of the $\Lambda_c/\sqrt{c}$ lines, increases from lithium to potassium. The weakest metallic uni-univalent salt in acetone is silver nitrate, which is only about 10% dissociated at $N/2000$. Certain mono- and di-substituted ammonium chlorides are also weak electrolytes.

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* The publication both of this paper and that of A. Unmack and E. Bullock [119] has been delayed owing to the preparation of this Report, but values from them have been included for the sake of completeness.

Ethylene Dichloride ($D = 10$).—The results are due to the work of Walden and Busch [85] and are restricted to salts with organic kations. None of the salts is a strong electrolyte, but the tetra-substituted ammonium salts are the most ionised. The degree of dissociation for these increases with the number of carbon atoms in the kation, and at $N/2000$ varies from 25% for tetraethylammonium picrate to 55% for tetra*iso*amylammonium picrate. The di- and tri-substituted ammonium salts, on the other hand, are very weak electrolytes and the degree of dissociation at $N/2000$ is less than 1% in all cases.

Tetrachloroethane ($D = 8$).—A few tetra-substituted ammonium salts have been measured in this solvent by Walden and H. Gloy [86] at concentrations below $N/10{,}000$. They find that all the salts are weak electrolytes, the strongest being only about 50% dissociated at $N/10{,}000$.

s-*Dichloroethylene* ($D = 7$, approx.).—The results in this solvent are also due to Walden and Gloy.[86] The work was mainly restricted to the di-, tri-, and tetra-*iso*amylammonium salts; all are weak electrolytes but the fully substituted salts are, as in other solvents, much more ionised than the other salts. At $N/1000$, the degree of dissociation for the fully substituted compounds is about 10%, while none of the other salts is more than 1% dissociated.

Summary of the Results for Uni-univalent Salts in Various Solvents.—There is ample evidence of the close approach to a linear relation between Λ_c and $\sqrt{c}$ in a number of solvents as required by the Debye and Hückel theory, and the extent of the agreement between the measured slope of the conductivity in different solvents with that calculated by the Debye–Hückel–Onsager equation is shown in Table I, which gives, for a number of typical salts, the percentage deviation, $100(x_{\text{obs.}} - x_{\text{calc.}})/x_{\text{calc.}}$.

It will be seen that in each of the first five solvents there are some salts which show close agreement with theory, and it is significant that with few exceptions any large deviation from ideal behaviour is in the direction that can be explained by ionic association, namely that $x_{\text{obs.}}$ is greater than $x_{\text{calc.}}$ This body of evidence appears to be sufficient to justify the use of the Debye–Hückel–Onsager equation as a working hypothesis to represent the behaviour of an ideal electrolyte, and we have therefore a new means of investigating the degree of association of electrolytes in the dilute range where the theory can be applied with safety.

TABLE I.

Percentage deviations from Onsager's equation at 25°.

	Water.*	MeOH.	EtOH.	$CH_3 \cdot NO_2$.	$CH_3 \cdot CN$.	Acetone.
$\eta^{25°}$	0·01056	0·00545	0·01080	0·00627	—	0·00308
$D^{25°}$	81·3	30·3	25	37	36	21
LiCNS ...	17†	− 1	18	weak	—	[960]
NaCNS ...	3†	− 2	24	weak	—	250
KCNS	6†	0	37	188	—	122
RbCNS ...	—	0	54	—	—	122
CsCNS ...	− 6†	10	78	—	—	124
LiI	—	—	10	300	—	96
KI	− 8·8	− 10	38	73	17	58
$LiClO_4$ ...	− 12	− 2	10	430	—	54
$NaClO_4$ ...	15‡	8	52	175	—	73
LiPic	− 32	—	16	—	410	270
NaPic	—	3	104	—	106	190
$AgNO_3$ ...	15	70	130	—	84	weak
NEt_4Pic ...	− 10	17	75	− 1·5	6	34
NEt_4I	—	33	102	2	5·7	98
NEt_4ClO_4	—	40	164	9	24	68

* All values for water are at 18°.

† These values refer to the chlorides, not to the thiocyanates, as no accurate measurements of the latter have been made in water.

‡ This value is for potassium perchlorate.

As Walden [87] and Ulich [88] have pointed out, a general comparison of the conductivity results reveals a most striking contrast between water and the two lowest alcohols and the non-hydroxylic solvents. In water, all uni-univalent salts are strong electrolytes, and this is true also of methyl and ethyl alcohol, but in these solvents individual differences begin to make their appearance as the interionic forces increase and the varying tendencies to association are brought to light. Much of the extraordinary regularity of the conductivity curves in Kohlrausch's classic diagram [89] for aqueous solutions disappears when the same values are plotted for the alcohols. Nevertheless, the hydroxylic solvents favour complete ionisation and suppress the individual tendencies of electrolytes, their effect being described by Ulich as " nivellierend " or levelling, as opposed to the non-hydroxylic solvents such as nitromethane, nitrobenzene, acetonitrile, and acetone (described by Ulich as " differenzierend "), in which uni-univalent salts may be weak electrolytes. This is not the result of larger interionic forces, since the first three have larger dielectric constants than methyl alcohol.

Another difference between the two classes of solvent is that in the alcohols the tendency to association in any series of salts with the same anion increases with the atomic number of the kation, while in the non-hydroxylic solvents the association increases in the order $K^{\cdot} < Na^{\cdot} < Li^{\cdot}$ (with the possible exception of the perchlorates in acetone), and the lithium salt is often a weak electrolyte when the potassium salt is highly ionised. The relative tendencies of the anions to promote ionic association are not quite so marked but are roughly in the order

$$(ClO_4', Pic', I') < (Br', NO_3') < (Cl', CNS')$$

although there are variations from this scheme.

In the alcohols, the tetra-substituted ammonium salts show the maximum deviation from the theoretical slope, while in the non-hydroxylic solvents they give results which agree most closely with theory.

In each type of solvent the general tendency to association increases as the dielectric constant decreases, though this is not always true, as a few salts are more highly dissociated in acetone than in nitromethane.

It will thus be seen that a purely physical theory such as that of Debye, Hückel, and Onsager, while it is of great value in predicting the behaviour of an ideal electrolyte, is far from giving a complete picture of the behaviour of electrolytic solutions. The chemical nature of the solvent molecules and of the ions themselves is often the predominant factor.

The Conductivity of Acids in Different Solvents.—Acids are treated separately, as they hold a special place among electrolytes owing to the unique nature of the hydrogen ion. Taking first the acids which are strong electrolytes in water, the experimental work in aqueous solutions is not as accurate as that for salts, since the difficulties of investigating acids, especially in dilute solution, are so much greater. H. C. Parker [90] made accurate measurements of hydrochloric acid and the results obey the square-root relation except in very dilute solution, where the deviations are almost certainly due to reaction with solvent impurities. Onsager [18] has shown that the slope of the line is in good agreement with that calculated theoretically. Davies [91] pointed out that iodic acid is not completely dissociated even in dilute solution, and this is confirmed by a comparison with Onsager's equation.

Goldschmidt and Dahll [64] measured the conductivity of hydrogen chloride, bromide, and iodide in methyl and ethyl alcohols, and the measurements of the first were recently extended to more dilute solutions by Thomas and Marum.[70] All three halogen acids are found to be highly dissociated in both solvents, although in Goldschmidt's work the points do not lie on straight lines when Λ_c is plotted against $\sqrt{c}$. This may be due, however, to the use of the Ostwald method of dilution. The work on hydrogen chloride was repeated by Murray-Rust and Hartley,[92] who also investigated a number of other acids which are strong electrolytes in water. Of these, hydrochloric, perchloric, ethylsulphuric, and benzenesulphonic acids are strong electrolytes in both alcohols and conform to the square-root relation. The deviations from equation (6) are greater in ethyl alcohol, showing that there is more ionic association in this solvent than in methyl alcohol; the deviation is smallest for hydrogen chloride in methyl alcohol, which is in quite good agreement with theory. Nitric and thiocyanic acids are weak acids in ethyl alcohol and have dissociation constants of the order of 10^{-4}, while the tendency of iodic acid to associate in aqueous solution is accentuated in methyl alcohol, in which it has a dissociation constant of about 10^{-8}.

Very few measurements of acids have been made in non-hydroxylic solvents. In nitromethane, Wright, Murray-Rust, and Hartley [78] have shown that perchloric acid is the only one that is highly dissociated, other acids which are strong in the alcohols, such as hydrogen chloride and benzenesulphonic acid, being very weak electrolytes; and the same is true for nitric and thiocyanic acids. Ross Kane [84] has found similar results in acetone, in which perchloric acid is the only strong acid and conforms to the square-root relation, and in nitrobenzene [80] it is a much stronger electrolyte than any other acid measured, although in this solvent it is only about 55% dissociated at $N/1000$. These results further emphasise the fact that the degree of ionisation of an electrolyte in any solvent is controlled by the chemical properties of the solvent as well as by its dielectric constant. They also illustrate the relative reluctance of the perchlorate ion to form covalent links with a kation in solution.

Turning now to acids which are weak in water, Goldschmidt and his co-workers [71, 93] have measured the conductivity of a number of these in methyl and ethyl alcohols, and find that their dissociation constants are considerably lower in these solvents than in water, the mean ratios of the dissociation constants in the different solvents being

$$K_{\mathrm{H_2O}}/K_{\mathrm{MeOH}} = 10^4 \qquad K_{\mathrm{MeOH}}/K_{\mathrm{EtOH}} = 10^4$$

H. Hunt and H. T. Briscoe [94] have measured the conductivity of a number of weak acids in water and the four lowest primary alcohols and also in acetone. They find that the conductivity of the acids decreases with increasing molecular weight of the alcohol, but there is more difference between ethyl and propyl alcohols than between propyl and butyl alcohols.

The calculation of dissociation constants of weak electrolytes has been modified by the new theory, as two corrections have to be made in the expression $\Lambda_c^2 \,.\, c/\Lambda_0(\Lambda_0 - \Lambda_c)$.

(1) The denominator in the expression Λ_c/Λ_0 does not allow for the fall in mobility with increasing concentration owing to the interionic forces, and the true degree of dissociation is given by $\alpha = \Lambda_c/\Lambda'$ where Λ' is the conductivity which the electrolyte would have at concentration c if it were completely dissociated. This can be calculated from the Debye–Hückel–Onsager equation.

(2) The ionic concentrations in the expression for the dissociation constant should be multiplied by the activity coefficients.

The final expression for the true dissociation constant is

$$K = \alpha^2 f^2 c/(1 - \alpha),$$

where f is the mean activity coefficient of the ions, and $\alpha = \Lambda_c/\Lambda'$ as above. This equation was applied to weak acids in water by D. A. MacInnes[95] and by M. S. Sherrill and A. A. Noyes,[96] though the calculation of α was made from experimental results for strong electrolytes, as Onsager's equation had not been published. This method of calculating K has been applied to salts in water by Davies,[63, 98] to uni-univalent salts in benzonitrile by Martin,[81] and to acids in methyl and ethyl alcohols by Murray-Rust and Hartley.[92]

Ionic Mobilities.

Determination of Values of Λ_0.—There are two main extrapolation formulæ by which the equivalent conductivity at infinite dilution of strong electrolytes has been obtained. Most authors use the square-root relation $\Lambda_c = \Lambda_0 - x\sqrt{c}$, which has theoretical support and represents the behaviour of many uni-univalent electrolytes in dilute solution, both in water and in non-aqueous solvents, although in the latter the experimental slopes are often greater than those calculated from Onsager's expression. In this case the theoretical justification for the procedure is removed, and the points on the graph might be expected to lie on a curve which would become tangential to the theoretical slope in very dilute solution, but as a general rule they do lie on a straight line even when the slope is considerably greater than the theoretical value, as for example in acetone. A curvature in dilute solution is sometimes obtained experimentally, even when the linear portion at higher concentrations does not deviate widely from equation (6), but this is probably due to experimental error, arising from reaction of the solute with solvent impurities or from some other cause. The justification for this view is that the degree of curvature is dependent on the nature of the solute and not on the slope of the linear portion, and that the deviation from the straight line is greatest when solvent of high specific conductivity is used. In some unfavourable cases the curvature is so pronounced that a maximum is obtained, as in Gibbons and Getman's curve for silver nitrate in methyl alcohol.[112] In a few cases, however, when the electrolyte is of an intermediate nature, a curvature of the $\Lambda_c/\sqrt{c}$ line is obtained which is probably due to decreased association in dilute solution: examples of this are thallium chloride [18] and iodic acid [91] in water and silver perchlorate in nitrobenzene,[80] which give curves tending to become tangential to the Onsager slope at high dilutions.

It is clear, therefore, that extrapolation on the square-root basis may give values of Λ_0 which are too high when the slope of the line is greater than the theoretical value, as this method neglects the possibility of curvature in very dilute solutions; the value will be more nearly correct as the slope of the linear portion approaches more closely to the calculated value.

The other method of extrapolation is due to A. Ferguson and I. Vogel, [82, 99] who considered that a large number of electrolytes in water do not conform sufficiently closely to the square-root relation to justify its use as an extrapolation formula, and in a later paper have extended their calculation to methyl alcohol.[100] They use a modified form of the Storch equation, *viz.*, $\Lambda_c = \Lambda_0 - Bc^n$, and have worked out a graphical method for determining the arbitrary constants B and n. These values of n are different for each electrolyte and vary for water from 0·374 for potassium chloride to 0·97 for hydrochloric acid. A possible danger in using this method is that the value of n for any electrolyte may depend too much on the accuracy of the values of Λ_c in very dilute solution, which are particularly liable to error. For instance, the existence of a maximum at 0·0001N in the graph of Parker's results for hydrogen chloride in water [90] shows that they are affected by the presence of solvent impurities or some other cause. Ferguson and Vogel, however, arrive at a value of Λ_0 which is probably too low, since they have taken into account points below the straight line drawn through the values at concentrations greater than 0·0002N, although this has almost exactly the theoretical slope (compare Davies [97]). On the other hand, the method may be most useful when the extrapolation on the square-root basis is impossible owing to the curvature of the graph, as, for example, with solutions in benzonitrile.

The mobilities given on p. 351 are all calculated from values of Λ_0 found by extrapolation on the square-root basis, with the exception of those in benzonitrile and in nitromethane.

Transport Numbers.—In order to calculate the mobilities of individual ions from the equivalent conductivities at infinite dilution a knowledge of transport numbers is required. Since these vary with concentration, special importance attaches to the values in dilute solution, the determination of which involves considerable experimental difficulties. It is clear, however, from a collection of transport numbers such as that given by Kohlrausch and L. Holborn [101] that they tend to become constant in water as the concentration falls to 0·01N, and this is what might be expected on general grounds in dilute solutions. Further, Washburn's correction [102] for the differential shift of solvent with the ions during electrolysis brings the transport numbers of the alkali halides in 1·25N solution much nearer to their values at 0·01N and in the case of potassium chloride makes them identical, showing that the apparent variation with concentration is due in part to unequal solvation of the ions and not entirely to variations in their relative speeds at different concentrations.

Three methods of determination are available: (1) the analytical method of Hittorf, adapted for use in dilute solutions by B. D. Steele and R. B. Denison; [103] (2) the moving-boundary method of Denison and Steele [104] which has been elaborated lately by MacInnes and his co-workers [105] to give results of high precision, though it may be difficult to use at high dilutions; (3) the *E.M.F.* method, developed by D. A. MacInnes and J. A. Beattie [106] to give transport numbers at definite concentrations instead of mean values for a concentration range. The actual method of computation used by them implies a continuous variation of the value in dilute solution and seems therefore unsuitable for use in this region.

In aqueous solutions the three methods yield results that agree closely. The mobilities of ions at 18° in water are based on the transport number for the potassium ion in potassium chloride of 0·495. If the mobilities of other ions are calculated from conductivity results by means of this value, excellent agreement is found between the calculated and observed transport numbers.

D. A. MacInnes and I. A. Cowperthwaite [107] have pointed out that the agreement between the mobilities of the chloride ion determined from various univalent chlorides up to the dilutions of 0·1N is additional evidence of the existence of complete dissociation in aqueous solution; corresponding discrepancies in the case of some nitrates and iodates point to some measure of association in these solutions which is confirmed by other evidence.

In other solvents, transport data are much more scanty and much less consistent in dilute solutions. If the Hittorf method is used, the analysis of dilute solutions and the manipulation of volatile solvents offer considerable difficulties. For the *E.M.F.* method, electrodes reversible to both ions of the electrolyte are necessary and so measurements in the alcohols are practically limited to solutions of hydrogen chloride, since J. H. Wolfenden [108] and J. R.

Partington and H. G. Simpson [109] have shown that amalgam electrodes give anomalous results at low concentrations.

In methyl alcohol, G. Nonhebel and Hartley [110] measured the *E.M.F.* of hydrogen chloride cells with and without liquid junctions over a wide concentration range and found the transport number of the hydrion in dilute solution to be 0·735. Similar experiments by J. N. Pearce and H. B. Hart,[111] using amalgam electrodes, gave a transport number of the lithium ion in lithium chloride of 0·324, while V. L. Gibbons and F. H. Getman's [112] value for silver in silver nitrate, $n_{\mathrm{Ag}} = 0{\cdot}421$, obtained by the analytical method, agrees with the previous result, 0·428, of H. C. Jones and H. P. Bassett.[113]

In ethyl alcohol, J. R. Partington, G. F. Isaacs,[114] and H. G. Simpson [109] find that the transport numbers for the kations of sodium and potassium iodides are 0·418 and 0·450 respectively. They consider their measurements with amalgam electrodes to be unreliable at concentrations below 0·1*N*, and hence have calculated transport numbers from their measurements of the cells with liquid junctions alone, on the assumption that the ratio of the activity coefficient at two concentrations is equal to the ratio of the equivalent conductivities. For the transport number of lithium in lithium chloride, values ranging from 0·32 to 0·41 have been obtained, the most trustworthy of which is probably that of C. Drucker and R. Schingnitz,[115] *viz.*, 0·38. H. S. Harned and M. F. Fleysher [116] have found the transport number of the hydrion to be 0·755 at 0·002*N* from a study of hydrogen chloride concentration cells, while J. W. Woolcock, H. Hartley, and O. L. Hughes [117] by similar experiments obtained a value of 0·710. The former authors used MacInnes's method of calculation and so their numbers in the dilute range are probably too high.

Table II gives a comparison between the observed values of n_c in both alcohols, and the values calculated from the equivalent conductivities by means of the transport number of hydrogen chloride in dilute solution. The absence of any such concordance as exists

TABLE II.

Transport numbers.

		n_c in MeOH at 25°.			n_c in EtOH at 25°.	
Electrolyte.	Conc.	Obs.	Calc.	Conc.	Obs.	Calc.
HCl	0·001*N*	0·735 [110]	(0·735)	0·001*N*	0·710 [117]	(0·710)
				0·001*N*	0·755 [116]	
LiCl	0·006*N*	0·324 [111]	0·436	0·01*N*	0·38 [115]	0·376
NaI				0·001*N*	0·418 [109]	0·395
KI				0·001*N*	0·450 [114]	0·434
$AgNO_3$	0·04*N*	0·421 [112]	0·460	0·05*N*	0·397 [113]	0·387

in the data for aqueous solutions is at once apparent, although the agreement is better in ethyl than in methyl alcohol.

From a study of silver nitrate concentration cells with liquid junctions, F. K. V. Koch [118] found the transport number of the silver ion to be 0·458 in acetonitrile and 0·466 in benzonitrile. In other solvents, transport-number measurements are either entirely lacking or confined to strong solutions.

Walden's Rule.—The relation on which Walden and Ulich [10] have based the calculation of ionic mobilities in a number of organic solvents is that, for certain large organic ions, $l_0\eta$ is constant, where l_0 is the mobility of the ion and η the viscosity of the solvent. If the motion of the ion obeys Stokes's law or any other expression of the same form, *viz.*, velocity = (constant × force)/(ionic radius), then the constancy of the product $l_0\eta$ is a measure of the extent to which the ionic radius remains unaltered in different solvents. Walden and Ulich have shown that the product for a number of ions is practically constant over a wide range of temperature both in water and in other solvents, but Ulich's values for $l_0\eta$ for typical ions in water and the alcohols (Table III) show that for monatomic ions the values are roughly twice as great in water as in methyl alcohol and smaller again in ethyl alcohol, which may indicate a relation between the radius of the solvated ion and the molecular volume of the solvent. For organic ions, such as $NEt_4^{\cdot}$ and the picrate ion, the values of $l_0\eta$ are almost constant in the three solvents, which suggests the absence of solvation.

TABLE III.

Values of $l_0\eta$ *at* 25°.

	Water.	MeOH.	EtOH.
$K^{\cdot}$	0·68	0·30	0·26
$Na^{\cdot}$	0·46	0·26	0·24
$Li^{\cdot}$	0·35	0·22	0·19
$NEt_4^{\cdot}$	0·294	0·295	0·295
Cl'	0·69	0·29	0·23
Pic′	0·270	0·273	0·263

Walden has recently tested the accuracy of the rule by measuring the product $\Lambda_0\eta$ for a salt containing both a large kation and a large anion. Tetraethylammonium picrate, in particular, has been measured in a large number of solvents, and Walden finds that the product $\Lambda_0\eta$ is sensibly constant in each case and is close to the mean value 0·563 [85] at three different temperatures. Table IV gives Walden's values in a number of solvents at 25° (water, 18°).

The values given in brackets are due to other authors, and the constancy of $\Lambda_0\eta$ may not be quite so exact as Walden supposed.

TABLE IV.

Values of $\Lambda_0\eta$ for tetraethylammonium picrate.

	Water.	MeOH.	EtOH.	$CH_2 \cdot NO_2$.
Λ_0 …………	53·3	102·9 (108·5) [119]	51·5 (55·2) [73]	(93·5) [78]
η …………	0·01056	0·00546	0·01080	(0·00627)
$\Lambda_0\eta$ …………	0·563	0·562 (0·593)	0·557 (0·596)	(0·586)

	$CH_3 \cdot CN$.	$C_6H_5 \cdot NO_2$.	Acetone.	$CH_2Cl \cdot CH_2Cl$.
Λ_0 …………	163·8	(32·7) [80]	177·5	71·3
η …………	0·00344	(0·0183)	0·00316 (0·00308) [84]	0·00785
$\Lambda_0\eta$ …………	0·563	(0·598)	0·561 (0·550)	0·560

Further investigations are necessary to clear up these discrepancies, but in any case the rule is sufficiently closely obeyed to justify the use of this method of calculating mobilities from mean values of the product of l_0 and the viscosity of the solvent in cases where no other method is at present available.

Walden uses the mobility of the tetraethylammonium ion for this purpose, taking a mean value of 0·295 for $l_0\eta$; other authors have used the picrate ion with a value of 0·275.[78,80]

Table of Ionic Mobilities.—The investigations on which the values of ionic mobilities in Table V are based are as follows: In water the values given were calculated from Kohlrausch's values at 18°, his temperature coefficients [101] being used except in the case of numbers for which a special reference is given. In methyl alcohol, the values depend on the conductivity results of Frazer and Hartley [67] and the transport number of the hydrion in hydrogen chloride of 0·735; [110] and in ethyl alcohol, on the conductivity results of Barak [73] with the analogous transport number of 0·71.[117] In other solvents, the values have been calculated from Walden's rule; in nitromethane and acetone, from the picrate ion, taking $l_0\eta = 0{\cdot}275$, and in acetonitrile from $NEt_4^{\cdot}$, taking $l_0\eta = 0{\cdot}295$. The conductivity measurements were made in nitromethane by Wright, Murray-Rust, and Hartley,[78] in acetonitrile by Walden and Birr,[79] and in acetone by Ross Kane.[84] In the last solvent the values in brackets are taken from the results of Walden, Ulich, and Busch.[83]

The main points of interest arising out of the following table are: (1) the periodic increase in each solvent of the mobilities of the ions of the alkali metals with increasing atomic number, (2) the absence of such a general periodic relationship in the mobilities of the halogen ions, (3) the relatively large mobilities of a number of polyatomic ions as compared with monatomic ions in non-aqueous

TABLE V.

Ionic mobilities at 25°.

Ion.	Water.	MeOH.	EtOH.	$CH_3{\cdot}NO_2$.	$CH_3{\cdot}CN$.	Acetone.
η_{25° =	0·00895	0·00545	0·01080	0·00627	0·00344	0·00308
$H^{\cdot}$	351[90]	142	59·5	63	—	88
$Li^{\cdot}$	39·6	39·7	14·9	55	59	75 (68)
$Na^{\cdot}$	51·0	45·7	18·7	58	70	80 (65)
$K^{\cdot}$	74·2	53·7	22·0	60	86	82 (67)
$Rb^{\cdot}$	77·6	57·4	23·6	—	—	86
$Cs^{\cdot}$	78·1	62·3	25·5	—	—	88
$NH_4^{\cdot}$ ...	74·0	57·9	19·2	64	—	98
$NEt_4^{\cdot}$ ...	33·0[10]	62[119] (53)[66]	28·4	49·5	86†	90 (90)
$Ag^{\cdot}$	63·0	50·3[69]	17·5	52	85	88
Cl'	75·4	51·3	24·3	—	89	111 (108)
Br'	77·7	55·5	25·8	—	96	113
I'	76·4	61	28·7	62	101	110
ClO_4' ...	67[60]	70·9[69]	33·8	64	104	117 (119)
Pic′	30·7[10]	46·7	26·8	44 *	78	87*
CNS′ ...	65·4	61[68]	29·2	70	—	123
NO_3' ...	70·6	60·8	28·1	64·5	104	120

* Calculated from $l_0\eta = 0{\cdot}275$.
† Calculated from $l_0\eta = 0{\cdot}295$.

solvents, the most noticeable being $NEt_4^{\cdot}$ and ClO_4'. Varying degrees of solvation are generally thought to be responsible for these differences, and the high mobilities of ions with symmetrical structures such as $NEt_4^{\cdot}$ and ClO_4' are suggestive in this respect.

The hydrogen ion occupies a special position in view of its abnormal mobility in hydroxylic solvents. A chain mechanism involving the transference of a proton from an oxonium ion, $(OH_3)^{\cdot}$, to a water molecule has been suggested to explain this, and Hückel[120] has made a mathematical analysis of the problem with especial reference to the temperature coefficients of the mobilities of the hydrogen ion and of the hydroxyl ion, for which a similar chain mechanism has been assumed. In acetone and nitromethane, on the other hand, the hydrogen ion does not possess an abnormal mobility; in these solvents the formation of complexes similar to $(OH_3)^{\cdot}$ and $ROH_2^{\cdot}$ is unlikely and consequently the mobility of the hydrion cannot be increased by proton transference.

The Solvation of Ions and its Relation to Ionic Dissociation.

R. Fricke[121] has given an excellent summary of the work on the solvation of ions up to 1922. Since then, much attention has been given to the question of solvation but, although the evidence from various quarters for its existence and its influence on ionic dissociation has been considerably strengthened, it cannot be said that our views about the nature of solvation have become much more definite or have assumed a more quantitative form.

H. Remy [122] and G. Baborovský [123] have investigated independently the movement of water with ions during electrolysis by measuring the shift of solution when the anode and cathode compartments are separated by a membrane. Their results are in fairly good agreement with one another and also with those of Washburn,[102] who used an electrically inert reference substance. Washburn's experiments have received further confirmation from M. Taylor and E. W. Sawyer,[124] who used urea as a reference substance instead of raffinose. Remy, on the assumption that certain large organic ions are not solvated, has estimated the degree of hydration of a number of ions, his values varying from $12H_2O$ for $Li^\bullet$ to $4H_2O$ for $Cs^\bullet$. Ulich [10] made a similar estimate, both in water and in other solvents, by calculating the number of solvent molecules required to account for the difference in size between the solvated ion calculated from its mobility by Stokes's equation and the same ion in a crystal lattice. His numbers are smaller than Remy's, *e.g.*, 6—$7H_2O$ for $Li^\bullet$. He pointed out that the relative solvation of different ions is likely to be affected by steric influences resulting from the dipole configuration of the solvent molecules.

The molecules of solvent may be held by the ions simply by virtue of their dipole character, or they may be held by co-ordinate linkages. Schmick [29] has developed the work of M. Born [125] on the effect of the neighbouring dipole molecules on the mobility of an ion, and has shown that in the case of water the dipoles would be so strongly held by small ions that they would lose all degrees of freedom. N. V. Sidgwick [126] has considered solvation from the electronic standpoint and has emphasised the importance of the donor and acceptor properties of hydroxylic solvents in enabling them to form co-ordinate links with both anions and kations. He also pointed out that the relative solvation of the ions of the alkali metals is in accordance with K. Fajans' [127] theory of the influence of the size of an ion on its power to deform the electron orbits of a neighbouring ion or molecule.

Bjerrum [26] has considered the effect of ionic size on the probability of the formation of ion pairs, which would contribute nothing to the conductivity of a solution, and has shown that, if the sum of the radii of two ions is below a certain value, the number of ion pairs will increase rapidly. The Debye–Hückel theory takes no account of the association of ions, and the conductivity data for any series of salts of the alkali metals in methyl or ethyl alcohol show an increasing deviation from theory with increasing atomic number, corresponding to an increase in association with diminution in size of the solvated ion. Hence the solvation of the ions has an important effect in reducing association by preventing the ions from coming near enough together to form ion pairs. It is significant that, in non-hydroxylic solvents such as nitromethane, which can only form a co-ordinate link with the kation, most lithium salts are weak, in spite of the high dipole moment of the solvent molecules, indicating the importance of a chemical link between the anion and solvent in preventing ionic association.

Ulich [88] has pointed out that valuable evidence as to the dependence of ionisation on the properties of the solvent molecules has been obtained from the effect of the presence of small quantities of water (0·5% or less) on the conductivity of solutions in other solvents. The main change in the physical properties of the solvent produced by the addition of water is a change in viscosity, which should produce a corresponding alteration in the conductivity if no other changes occur. The observed effects vary greatly with the character of the electrolyte, as is seen from the following details.

(a) *Strong salts.* In methyl [128, 68] and ethyl [128, 73] alcohols, and also in acetone [84] and nitromethane,[78] the change in conductivity of uni-univalent salts is of the same order as the change in viscosity, as would be expected if dissociation were approximately complete.

(b) *Strong acids.* Goldschmidt and H. Aarflot [128] and also Murray-Rust and Hartley [92] have shown that the conductivity of strong acids in methyl and ethyl alcohols is decreased to a much greater extent than could be expected from the viscosity change. This is probably due to a decrease of the abnormal mobility of the hydrogen ion, and suggests that the greater affinity of the proton for the water molecule hinders the transference of the proton from one alcohol molecule to another. In acetone, on the other hand,[84] in which the hydrogen ion does not possess an abnormally high mobility, the change of conductivity on addition of water is of the same order as the change of viscosity.

(c) *Weak electrolytes.* The addition of water to the solution of a weak electrolyte in a non-aqueous solvent practically always increases the conductivity to a much greater extent than could possibly be explained by the change in dielectric constant. This has been observed for weak acids in the alcohols,[129, 92] and also for weak acids and weak salts in nitromethane [78] and in acetone.[84] For instance, in nitromethane the addition of 0·1% of water to a

$0{\cdot}002N$ solution of lithium thiocyanate raises the conductivity by 60%, the decrease of viscosity being only 0·3%.

The solvent therefore affects the conductivity of an electrolyte dissolved in it in a variety of ways. First, by the magnitude of its dielectric constant it determines the force of attraction between the ions and the energy needed to separate them. Then, the solvation of the ions appears to exert a decisive influence on the extent to which they form ion pairs or undissociated molecules, and in this respect the power of the solvent molecules to co-ordinate with both ions appears to be even more important than their dipole character. And lastly, the mobilities of the ions are determined by the viscosity of the solvent and by the extent of their solvation. The problem of the immediate future is to discover the precise nature and extent of the solvent atmosphere around the ions which exerts such an important influence on their properties.

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ERRATA.

THIS VOL.

Page	Line	
88	13*	*delete* "acetaldehyde."
91	15—14*	*for* "1 : 3 : 3-triphenylhydrindene" *read* "1 : 3 : 3-triphenyl-1-methylhydrindene."

* From bottom.

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